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DEVELOPMENT AND EVALUATION OF METHODS FOR TOTAL ORGANIC HALIDE AND PURGEABLE ORGANIC HALIDE IN WASTEWATER

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This report describes a series of studies involving the use of "surrogate" methods fo the determination of total organic halides (TOX), purgeable organic halides (POX), an solvent extractable organic halides (EOX), in wastewater and solid wastes. A pyrolysis/microcoulometric system was used as the analytical detection device for all studies.

Method performance data are presented for the various surrogate methods. The results obtained using the surrogate methods were compared to those obtained using compound-specific methods based on gas chromatography (GC) or combined gas chromatography-mass spectrometry (GC/MS). The advantages and limitations of using th surrogate methods in place of more sophisticated procedures are discussed.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

Under authority of Sections 304(h) and 501(a) of the Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977, the U.S. Environmental Protection Agency (U.S. EPA) is required to promulgate guidelines establishing test procedures for the analysis of pollutants. This report represents an evaluation of various procedures for the determination of organic halides in industrial wastewaters and solid samples as a group parameter.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and
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ABSTRACT

Various methods for determining total purgeable and nonpurgeable organic halides in wastewater have been reviewed. Two approaches, digestion with sodium biphenyl followed by colorimetric detection, and combustion followed by microcoulometric titration, were selected for laboratory evaluation. The latter approach involved the use of a commercial instrument (Dohrmann Model DX-20) which had been designed specifically for the separate analysis of purgeable organic halide (POX) and total organic halide (TOX using carbon adsorption).

The microcoulometric titration approach was found to be simpler to conduct and more precise than the sodium biphenyl digestion approach. Surrogate methods for POX and TOX in water and extractable organic halide (EOX) in water and solids were evaluated for a number of wastewater and solid samples. The results obtained using the POX surrogate method generally agreed within a factor of two with the results obtained by U.S. EPA Method 624 (GC/MS using the purge and trap technique). TOX results were generally much higher than results obtained by solvent extraction--GC methods (U.S. EPA Method 625 and/or 612).

The EOX approach, using the Dohrmann DX-20, involved significant modification of the sample inlet system of the instrument to allow the injection of 5-25 μL volumes of solvent directly into the combustion furnace. Precise and accurate determination of the priority pollutant organic halides was obtained using this approach.

This report was submitted in partial fulfillment of Contract No. 68-03-2984 by Battelle Columbus Laboratories under the sponsorship of the U.S. EPA. This report covers the period September 12, 1980 to October 15, 1981 and the work was completed as of October 15, 1981.

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SECTION 1

INTRODUCTION

The original objective of this program was to develop simplified group test procedures determining purgeable and nonpurgeable halide priority pollutants in wastewater. Specific compounds of interest in these two groups are listed in Table 1. Existing U.S. EPA Methods 601 and 612 (1) are currently used to detect purgeable and nonpurgeable organic priority pollutants, respectively. These methods involve the use of gas chromatography with halide specific detectors. Methods using gas chromatography/mass spectrometry (GC/MS), namely U.S. EPA Methods 624 and 625 (1), are also used to determine these compounds. The surrogate methods are designed to serve as pollutant-level indicators which, in many situations, can be used in place of the more specific "600" methods. The use of surrogate methods is primarily intended to reduce the cost of analysis associated with pollutant monitoring programs.

The requirements which such surrogate methods are expected to meet are given below. These objectives are designed to serve as general guidance and should not be viewed as rigid requirements. Obviously, each laboratory situation will require different aspects of these objectives to be emphasized more than others.

1. Quantification shall be positively correlated to that produced by the "600" methods (as the sum of the individual pollutants).

2. The method shall have the ability to stand alone as a reliable indicator of pollutant level.

3. The cost shall be no more than one-half of that using the appropriate "600" GC or GC/MS methods.

4. Response shall be class-specific, producing a very low frequency of false responses.

5. Responses need not be produced for individual pollutants.

6. Quantification shall produce a numerical value (rather than a range).

7. Detection limit shall be at least 1 μg/L.

8. Recovery shall be 70% or greater for the priority pollutants in the category.

9. The relative precision (as relative standard deviation) of replicate determinations shall be less than 50%.

10. Ruggedness shall be maximized.

The major objective of this program was to select, evaluate, and validate the methods which best meet the listed requirements for the priority pollutant organic halides. To accomplish this objective, a literature survey was conducted to formulate the most logical approach to meet these goals. The original objectives of this program were modified in that the range of compounds of interest was expanded to include purgeable organic halides and total organic halides in general, rather than being limited to the priority pollutants. This modification in the objectives significantly impacted the experimental design of the study as described in this report. Specifically, the impact on the study was the selection of generally applicable isolation procedures (i.e., charcoal adsorption) over more selective isolation procedures (i.e., solvent extraction). The former technique will isolate most organic halides whereas the latter technique, while adequately isolating priority pollutant organic halides, would not isolate polar organic halides as readily from aqueous matrices.

Two candidate approaches, reaction with sodium biphenyl (SBP) reagent followed by chloride determination using colorimetry and pyrolysis/microcoulometric titration, were selected for laboratory evaluation. Various means of sample preparation (carbon adsorption, solvent extraction, inert gas purging) were evaluated for use in conjunction with the microcoulometric titration approach. U.S. EPA Method 450.1 (Appendix C) was chosen as a possible approach for determining TOX in wastewater. While this method was written for drinking water analysis, only minor modifications appeared to be necessary for application to wastewater analysis.

TABLE 1. PRIORITY POLLUTANT ORGANIC HALIDES

Purgeable Organic Halides

Bromodichloromethane
Bromoform
Bromomethane
Carbon tetrachloride
Chlorobenzene
Chloroethane
2-Chloroethylvinyl ether
Chloroform
Chloromethane
Dibromochloromethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1-3-Dichloropropene
Methylene chloride
1,1,2,2-Tetrachloroethane
Tetrachloroethene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
Vinyl chloride

Nonpurgeable (Extractable) Organic Halides

1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachloroethane
1,2-Dichlorobenzene
Hexachlorobutadiene
1,2,4-Trichlorobenzene
2-Chloronaphthalene
Hexachlorobenzene

SECTION 2

CONCLUSIONS

This study has resulted in the development and evaluation of methods for POX in wastewater, TOX in wastewater, EOX in wastewater, and EOX in solids. Conclusions which can be made concerning the results of this study are summarized below:

- The SBP digestion approach is not as convenient to use nor as precise as the combustion/microcoulometric titration approach.
- The surrogate POX method gives results within a factor of two of those obtained by U.S. EPA Method 624 and for a number of wastewater samples agreement was within ± 25%. Agreement was generally very good for samples where the majority of the POX was represented by a single component. This degree of correlation appears to make the surrogate method a useful indicator of volatile organic halide pollution, although its applicability to any specific wastewaters should be evaluated before the surrogate method data is used by itself as a quantitative indicator.
- The TOX method (U.S. EPA Method 450.1, with minor modifications as described in the body of this report) gave precise results and good recoveries of spike components for all of the wastewaters tested. However, the TOX values were generally much greater than the sum of EOX (U.S. EPA Method 625) and POX (U.S. EPA Method 624) values. This result indicates that a large quantity of organic halides are present in the samples which are carbon adsorbable but not solvent extractable or recoverable. Data for backup cartridges indicate that inorganic halide adsorption is not significant, in spite of the high level of inorganic halide present in many of the samples. The nitrate washing step in the procedure appears to be very effective in removing inorganic halide interferences.
- The EOX method for water appears to be useful for the precise and accurate determination of the semivolatile priority pollutants listed in Table 1, and other readily

extracted organic halides (e.g., PCBs, chlorinated pesticides). However, this approach does not detect polar, nonextractable organic halides which are detected by the TOX carbon adsorption approach. This feature of the method is advantageous if the selective detection of nonpolar organic halides, such as the priority pollutants, is of interest, but undesirable if the TOX concentration is of interest.

- The EOX method for solids appears to work quite well for a variety of types of solids (e.g., soils, solid wastes, suspended solids contained in wastewater). However, because of the diversity of solid sample properties which are potentially of interest, the applicability of this approach to any specific sample needs to be evaluated before the surrogate method data can be used by itself with a high degree of confidence. Additional extraction solvents and other experimental parameters for this method should be explored before widespread use of the method occurs.

SECTION 3

RECOMMENDATIONS

Further evaluation of the surrogate methods developed and/or evaluated in this study is necessary in order to establish their applicability to the many matrices of interest. In certain instances, the operating parameters of the method should be evaluated more extensively than was possible in this study. For example, the reasons for the incomplete recovery observed for purgeable organic halides, especially at low concentrations, should be explored. The effects of such parameters as furnace temperature, purge temperature, purge flow rate, etc., should be systematically evaluated.

The SBP procedure was not explored in detail in this study because of the advantages described for the microcoulometric titration approach. However, in certain instances (i.e., where only a few samples are to be analyzed), this approach may be more cost effective than the microcoulometric approach because of the need to purchase instrumentation for the latter approach. Consequently, further evaluation of the SBP digestion approach may be warranted.

SECTION 4

LITERATURE REVIEW

A thorough review of the scientific literature revealed that virtually all of the quantitative organic halide detection methods fall into one of the following categories:

- Direct measurement of the halogen element in the organic molecule without need for conversion to other forms, e.g., X-ray fluorescence (XRF) and neutron activation analysis (NAA).

- Specific detection of the intact organic halides, e.g., the Hall detector and the electron capture detector which are used in gas chromatography.

- Cleavage of the halogen atom from the organic molecule and subsequent detection of the liberated halide, e.g., combustion, oxidation, and sodium reaction methods.

- Derivatization reactions followed by spectrophotometric analysis, e.g., group specific reactions.

These methods are applicable to both POX and nonpurgeable organic halides (NPOX), with only the method of sample preparation differing for the two groups of compounds. A summary of the available methods for organohalide determination is given in Table 2. Many of the methods listed in Table 2 involve conversion to inorganic halide and subsequent detection of the free halide. Methods for detecting inorganic halide are summarized in Table 3.

The XRF and NAA were not considered for use as the surrogate method because of the lack of general availability and high costs associated with this instrumentation. However, these instrumental approaches appear to be capable of accurately determining organic halide with a relatively low cost per analysis, and if low cost versions of these instruments become available, these approaches may become generally useful. The ability of these methods to distinguish the various halides (e.g., chloride, bromide, iodide) is an advantage not found in many of the other approaches.

Gas chromatography with specific detectors (Hall and electron capture) and GC/MS are used in the "600" methods, as discussed in the introduction. One possible approach as a surrogate for organic halide is the use of halide specific GC detectors, particularly the Hall detector, without prior GC

TABLE 2. SUMMARY OF REFERENCES ON QUANTITATIVE DETECTION OF ORGANIC HALOGEN COMPOUNDS

	Method	Application	Sample Preparation	Approximate Detection Limit in Sample	References	Comments
1.	X-Ray Fluorescence	Total halogen (by element)	Extraction with organic solvent	1-10 µg/L	2,3	Not suitable because of high initial investment(∿50-100K).
2.	Neutron Activation	Total halogen (by element)	Extraction with organic solvent	∿1 µg/L for Cl	4	Not suitable because of lack of availability in standard laboratories.
3.	Hall Detector and Electron Capture Detector	Specific detection of halogenated compounds separated by GC	Extraction or adsorption	∿1-10 µg/L	5,6	Not suitable because of need for GC system. Response dependent on type of organic halide (EC only)
4.	GC/MS	Specific detection of halogenated compounds separated by GC	Extraction	∿1 µg/L	7,8	Initial investment too high.
5.	Parr Bomb	Conversion of organic halides to inorganic halides	Extraction or adsorption	∿0.05-1mg/L	9,10,11,12	Requires special safety precautions. Oxidation of limited amounts of organic extract (<1 mL). High contamination risk.
6.	Schoeniger Combustion	Conversion of organic halides to inorganic halides	Extraction or adsorption	1-5 mg/L	13	Requires special safety precautions. Only for small amounts.

TABLE 2. (Continued)

	Method	Application	Sample Preparation	Approximate Detection Limit in Sample	References	Comments
7.	Oxidation, Furnace Tube	Conversion of organic halides to inorganic halides	Adsorption	$\sim$1 µg/L	14–17	Currently in use in EPA Method 450.1
8.	Oxidation, using oxidizing agents	Conversion of organic halide to chlorine	Acid digestion	$\sim$50 mg/L	18,19	Lacks sensitivity and reproducibility.
9.	Reaction with sodium or sodium based reagents	Conversion of organic halides to inorganic halides	Extraction	$\sim$1-10 µg/L	20–25	Has not been evaluated at low levels.
10.	Lamp Method	Conversion of organic halides to inorganic halides	Extraction	$\sim$0.1 -1 mg/L	26,27	Time consuming unless burner is modified, high risk of contamination.
11.	Fujiwara Reaction	Specific color-reaction for organic halides	None	$\sim$1 mg/L	28,29	Reaction not specific enough. Many organic halides do not react.

TABLE 3. SUMMARY OF REFERENCES ON QUANTITATIVE DETECTION OF INORGANIC HALIDE

	Detection Method	Approximate Detection Limit in Sample	References	Comments
1.	Titration with $AgNO_3$ or $Hg(NO_3)_2$	$\sim$1-10 mg/L	30-41	Time consuming. Detection limit too high.
2.	Potentiometric microtitration ($AgNO_3$ or $Ag(ClO_4)$)	$\sim$1 mg/L	42	Time consuming. Detection limit too high.
3.	Microcoulometric titration	$\sim$1 µg/L	14-17	Suitable method: fast; low detection limit; equal response for halides; can be automated. However, does not differentiate between halides.
4.	Ion-selective electrodes	0.01-5 mg/L	30,43,44	Inexpensive; sensitive; differentiation between halides possible with separate electrodes for each halide. However, bromide and iodide are strong interferences for the chloride electrode, therefore unambigous interpretation of the Cl-data not possible in presence of Br^- and/or I^-.
5.	Ion chromatography	1-5 µg/L	45	Very sensitive and selective; however, high initial costs; need for well-trained and experienced lab personnel.
6.	Colorimetric/UV-Vis Spectrophotometric method based on "Hg-Fe-Thiocyanate Method" (ASTM Method D512)	1-20 µg/L	30,46,47	Suitable method: fast; low detection limit; equal response for halides (not F^-). Does not differentiate between halides. Need for spectrophotometer.
7.	UV Spectrophotometric Method based on "Hg-Chloranilate Method"	0.05 mg/L	30,48	Fast; low detection limit; can not detect Br^- and I^-.

separation (i.e., direct introduction of the sample extract or purge stream). However, this approach has not been successfully employed to date. One major obstacle to successfully implementing this approach is that the Hall detector will respond slightly to most solvents and/or to impurities in the solvents; hence prior separation of the sample components from the solvent (e.g., using a GC column) is necessary.

Parr bomb and Schoeniger combustion flask approaches have not been evaluated at low levels, and are subject to halide contamination unless great care is taken. The Parr bomb procedure involves high pressure and temperature and hence special safety precautions must be taken.

Oxidation of the organic halide with MnO_2 and other chemical reagents to liberate free chlorine has not been successfully employed at low levels. Because of the poor detection limit and reproducibility, this approach does not appear very useful as a surrogate method.

Reaction with metallic sodium (sodium fusion) has been used as a qualitative test for organic halides for many years. However, a more convenient method for performing the same chemical reaction is to form an organic complex with the sodium metal in solution. Biphenyl and naphthalene have been used as the complexing agents with ethylene glycol ethers, such as ethylene glycol dimethyl ether (glyme) or tetrahydrofuran (THF) as the solvent. These reagents have been shown to quantitatively release virtually all organic halides to free inorganic halide. However, these methods have not been employed at low levels (e.g., less than 1 mg/L) and therefore the possibility for halide contamination of the reagent has not been explored. The instability of these reagents (shelf-lives of a few weeks) is another drawback, as are the safety problems associated with handling metallic sodium.

The "Lamp" method involves combustion (in air) of a solvent containing organic halides using a wick, collection of the combustion gases in an impinger, and determination of the halide content in the impinger. This method appears to be subject to contamination, making it unsuitable for trace analysis. Furthermore, because of the large volume of impinger liquid required (10-20 mL), a large amount of extract must be combusted, thus increasing the time required for complete combustion of the solvent. Colorimetric derivatization approaches such as the Fugiwara reaction have been found to be unsuitable as surrogate methods because of the wide differences in response between various compounds (28,29).

Several workers (14-17) have employed combined oxidation furnace/microcoulometric as a means for detecting total organic halides in environmental samples. In this approach the organic halides are isolated from the sample in some manner (e.g., carbon adsorption, solvent extraction, gas purging) and placed in an oxidation furnace. The combustion gases are then collected in a liquid medium (e.g., acetic acid) and the inorganic halide determined by titration with silver ion. A semiautomated system for conducting this determination has been developed and is commercially available (16). The primary advantages of this approach are good sensitivity, good reproducibility, and low background levels.

Based on careful study of the available information, two approaches were selected for laboratory evaluation and further development. These two approaches are:

- Oxidation/microcoulometric titration using a commercially available system.
- Reaction of the organic halides with SBP or similar reagents and detection of halide using the Hg-Fe-thiocyanate method (53).

A further consideration is the method to be used for the isolation of organic halides from the sample. For nonpurgeable materials the most commonly used methods are solvent extraction (49), resin sorption (50), and carbon adsorption (45). Since carbon adsorption is presently in use in U.S. EPA Method 450.1 for determining organic halides in drinking water, this approach was selected as the primary approach to be evaluated. However, solvent extraction is considered a useful alternative, depending on the range of compounds of interest.

For POX both purging (51), carbon adsorption (45), or solvent extraction (52) have been used. In the case of the SBP procedure solvent extraction is the only viable approach. However, for the combustion/microcoulometric titration approach purging appears to be most convenient since the oxidant gas can be passed through the sample directly into the furnace. Purging has the advantage that NPOX components do not interfere, as is the case with carbon adsorption or solvent extraction.

A considerable amount of work has been conducted by Dressman at U.S. EPA (14,45) and others (15,17,50) concerning the use of the microcoulometric titration approach, and the current version of instrumentation (16) reflects various improvements based on the results of that work. Since none of these studies investigated the applicability of the various approaches to the determination of organic halides in industrial wastewaters, the initial thrust of the current work was to apply the optimized procedures developed in the previous studies to a variety of industrial wastewater samples.

SECTION 5

EXPERIMENTAL

SODIUM BIPHENYL DETERMINATION APPROACH FOR DETERMINATION OF ORGANIC HALIDES IN WATER

This approach involved: (1) digestion of organic halides in an organic solvent by addition of a solution of the SBP complex; (2) quenching of the reaction by addition of water; and (3) determination of inorganic halide using a colorimetric procedure.

Two methods of preparing the SBP reagent were investigated. The first method (22) was as follows:

- Ten mL of dry toluene and 2.3 grams of sodium (freshly cut) were placed in a 50-mL three-necked flask equipped with a high speed stirrer, a reflux condensor, and a nitrogen inlet.
- A slow stream of nitrogen was passed over the solution while gently stirring and heating under reflux.
- When the sodium was molten, the solution was vigorously stirred until the sodium was finely dispersed, the stirrer was stopped, and the flask allowed to cool to room temperature.
- While maintaining a nitrogen atmosphere in both flasks, the suspension was transferred to a 500-mL flask, also equipped with a stirrer. A 175-mL volume of THF was then added and the mixture cooled to 5°C in an ice bath.
- The solution was then gently stirred, and a solution containing 16 grams of biphenyl in 25 mL of THF was added slowly under a nitrogen atmosphere. Care was taken to prevent the solution temperature from exceeding 10°C.
- When the addition was complete the mixture was stirred for 1 hour at 0-10°C. The reagent was stored in the flask, under a nitrogen atmosphere, and was purged with nitrogen whenever an aliquot of reagent was removed.

A second procedure for preparing the SBP reagent was found to give a more stable solution. This second procedure was as follows:

- One mL of glyme was placed in a three-neck flask equipped with a nitrogen inlet, and a reflux condensor with a calcium sulfate drying column on top. All operations were conducted under a nitrogen atmosphere.

- A 16-gram quantity of biphenyl dissolved in 25 mL of glyme was placed in the flask and 2.3 grams of finely divided, freshly cut sodium metal was added in 50-100 mg increments over a 2-hour period.

- The reaction mixture was stirred overnight after which time the flask was capped with ground glass stoppers and stored at 4°C. The reagent was purged with nitrogen whenever an aliquot of reagent was removed. Organic halides were isolated from the water sample by extraction of 100-mL aliquots of water with 1.5 mL of cyclohexane in a 100-mL volumetric flask. This procedure was employed in order to retain volatile organic halides in the extract.

The following procedure was used for the digestion of organic halides in sample extracts.

- The cyclohexane extract was placed in a 15-mL screw-capped centrifuge tube containing 1 gram of anhydrous sodium sulfate. The dried extract was removed and placed in a second clean, dry centrifuge tube. The sodium sulfate was rinsed with an additional 0.5-mL aliquot of cyclohexane, which was combined with the initial cyclohexane extract.

- Two mL of the SBP reagent were added to the cyclohexane extract, and the mixture was shaken for 1 minute. One mL of distilled water was added and the mixture was shaken for 1 minute. The aqueous phase was transferred to a clean, dry centrifuge tube. The transfer procedure was repeated twice using 1-mL aliquots of 3 M HNO_3, and these extracts were combined with the original aqueous extract.

- The aqueous solution was filtered through a 0.22-μm filter (Millipore type GS) to remove suspended biphenyl. The filter was rinsed with 5 mL of distilled water and the filtrate was diluted to a final volume of 25 mL.

- Each sample extract was split into two 12.5 mL portions, one of which was analyzed for Cl^- according to ASTM D 512C (53). The absorbance of the other portion of the extract was read at 463 nm, and this absorbance was subtracted from the absorbance recorded for the color developed portion. All absorbance measurements were conducted using a Beckman DU-2 spectrophotometer.

EVALUATION OF METHOD FOR POX IN WATER USING THE MICROCOULOMETRIC TITRATION APPROACH

This approach involved use of the Dohrmann Model DX-20 analyzer which is equipped with a special purging device. A simplified block diagram for this instrument is shown in Figure 1. For POX analysis a 10-mL, or smaller, aliquot of the water sample is placed in the purge device and a stream of CO_2 is passed through the purge tube. The purged components enter the combustion tube (held at 800°C) and are converted to the corresponding hydrogen halides.

The hydrogen halide combustion products are trapped in the microcoulometric titration cell, which uses 70% acetic acid in water as a solvent. The quantity of silver ion required to titrate all of the hydrogen halide generated during the purging cycle is integrated electronically and, through appropriate instrument calibration, is displayed directly as micrograms of chloride titrated. When brominated compounds are determined, the reading must be divided by 2.25 to compensate for the difference in equivalent weights between chloride and bromide. Since the instrument is calibrated in terms of chloride concentration (µg/L), false (low) reading will be obtained for samples containing brominated compounds. A detailed description of the POX surrogate method is given in Appendix A.

The sample preparation and workup steps were essentially identical to those specified in U.S. EPA Method 624 (1). The instrumental parameters used were those specified by the instrument manufacturer and are specified below:

- Sample Volume - 5 or 10 mL
- Purge Gas - CO_2, 99.9%
- Purge Time - 10 minutes
- Purge Temperature - 45°C
- Purge Gas Flow - 300 mL/minute
- Furnace Temperature - 800°C.

The primary objective of this portion of the study was to evaluate the applicability of the existing protocol (originally developed for drinking water analysis) to a number of industrial wastewaters. Consequently, only a few limited experiments were conducted wherein the instrumental parameters were adjusted to determine the effect on the results.

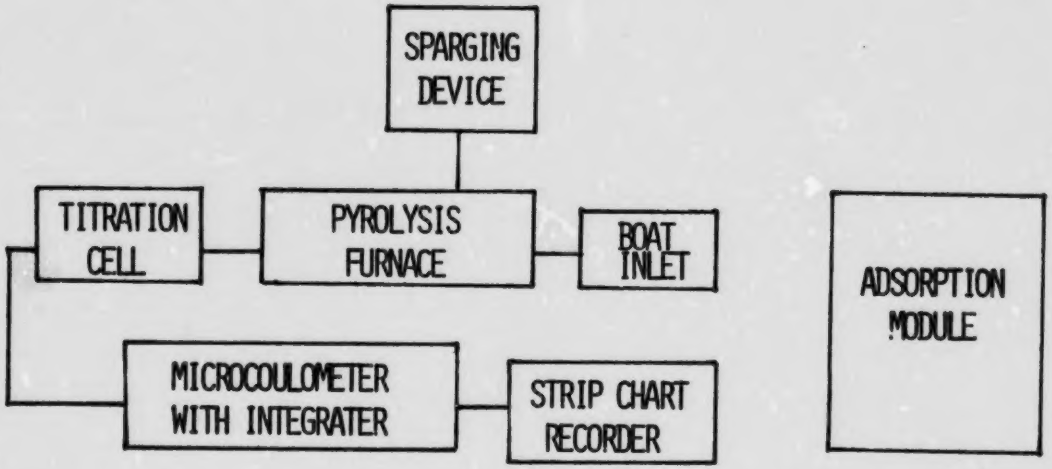
SPARGING DEVICE
TITRATION CELL
PYROLYSIS FURNACE
BOAT INLET
ADSORPTION MODULE
MICROCOULOMETER WITH INTEGRATER
STRIP CHART RECORDER

Figure 1. Dohrmann DX-20 TOX Analyzer.

Reagent water used in all phases of this study was obtained from a Millipore "Milli-Q" water purification system. The water was further purified by passing through a 2.5 cm x 50 cm column filled with 30-60 mesh granular activated charcoal just prior to use. All solvents used were distilled in glass grade from Burdick and Jackson. All chemical standards were purchased as the neat materials from Aldrich Chemical or Burdick and Jackson (e.g., chloroform) and were checked for purity using a GC equipped with a Hall detector.

Wastewater samples were collected in 1-gallon glass bottles with teflon-lined caps and without headspace. Two wastewater samples were shipped by the manufacturers in stainless steel drums (55 gallons) and several 1-liter aliquots were prepared (without headspace) immediately upon arrival at the laboratory. All samples were stored at 4°C prior to analysis. When replicate POX analyses were to be performed on a given water sample, a 1-liter aliquot was homogenized by manually shaking the bottle briefly and then pouring the sample into a number of 25-mL screw-capped vials with teflon-lined septum caps. These aliquots were treated exactly as specified in the POX procedure given in Appendix A. Spike components were added to the aliquot of sample contained in a 5 or 10-mL syringe by briefly opening the syringe valve and injecting the spike solution into the water using a 10 or 25-μL microsyringe.

Each sample evaluated using the POX surrogate method was also analyzed using U.S. EPA Method 624. This method involves purge and trap GC/MS analysis for volatile organic materials. The U.S. EPA Method 624 (1) protocol was followed exactly as written and a Firnigan 4000 mass spectrometer was used for the analyses. All GC/MS data were subjected to a reverse search and quantification routine for priority pollutants and were also inspected manually to determine whether other chlorinated components were present in the sample. Halogenated component concentrations were converted to μg/L as chloride and the total "POX" concentration determined by U.S. EPA Method 624 was compared to the POX surrogate value.

The method detection limit (MDL) for the surrogate method was determined using the U.S. EPA protocol given in Appendix B. The statistical basis for this protocol has been described in the literature (54). The MDL is defined as the measured quantity of material which can be reported with 99% confidence that the true analyte concentration is above zero. The MDL was determined by analyzing two or three reagent blanks and seven replicate aliquots of reagent water spiked with the analyte at a concentration of two to five times the estimated detection limit. The MDL was calculated, individually, for a number of POX compounds representing various compound classes.

DETERMINATION OF TOX BY CARBON ABSORPTION USING THE DOHRMANN DX-20 MICROCOULOMETRIC TITRATION SYSTEM

U.S. EPA Method 450.1, described in detail in Appendix C, was originally written for the determination of TOX in drinking water. Although this method will not distinguish purgeable and nonpurgeable organic halides, which was an objective of this study originally, the evaluation of the applicability of this method for wastewater analysis was deemed appropriate because of its current usage in support of various federal regulations. Briefly the method involves: (1) passing an acidified (with nitric acid) water sample through two granular activated charcoal (GAC) columns in series, (2) washing the cartridges with a KNO_3 solution to remove inorganic halide, and (3) combustion of the GAC in the Dohrmann apparatus, shown in Figure 1, using the boat entry system. The Dohrmann system provides capability for determining both POX and TOX. The combustion of the sample is accomplished in two stages. Volatile components are oxidized in a CO_2-rich atmosphere at a relatively low temperature (250°C) to prevent the conversion of bromine compounds to bromate (a nontitratable species). The less volatile components as well as the GAC are then combusted at 800°C in oxygen. Several modifications to the U.S. EPA Method 450.1 found to be necessary and/or advantageous when applying the method to wastewater analyses are described below.

Wastewater samples containing large amounts of suspended solid were centrifuged and the TOX determined separately on the supernatant and solid residue (solids analysis is described later). This step was necessary only in the case of one water sample ("aniline wastewater") for which the GAC columns were rapidly plugged if the solids were not removed.

Triplicate GAC blanks were analyzed each day. All GAC columns, including blanks, were flushed with 10 mL of methanol followed by 2 mL of water and 5 mL of KNO_3 solution (8.2 grams liter), just prior to use. The methanol rinse step was added to the procedure because it provided lower, more consistent GAC blank values.

The quantity of nitrate solution used to rinse the GAC column after passage of the sample was increased to 5 mL, since inorganic halide interference was severe for some wastewater samples when only a 2-mL volume (specified in U.S. EPA Method 450.1) was used. Otherwise, the sample preparation and instrumental parameters were identical to those specified in U.S. EPA Method 450.1.

An alternate approach to TOX analysis was evaluated wherein the GAC was added directly to the sample to form a slurry, and the GAC was subsequently removed by filtration (15). The slurry procedure involved the addition of GAC (40 mg) to a 50-mL sample in a 250-mL Erlenmeyer ground glass stoppered flask. The samples were shaken on a wrist-action shaker for 30 minutes. Following shaking, the samples were filtered through Millipore 13-mm cellulose acetate filters with an 8.0-micron pore size. The filter was held in a Swinney stainless steel filter holder and attached to a 20-mL syringe which was used to force the sample through the filter. After filtration, 10 mL of nitrate solution was added to the syringe and passed through the GAC to remove inorganic halides. The filter and GAC were then transferred to the DX-20 boat for analysis. In some cases the filter and GAC were analyzed separately.

DETERMINATION OF EXTRACTABLE ORGANIC HALIDES (EOX)

A method for determining EOX using the Dohrmann DX-20 system was evaluated using standard solutions and spiked reagent water and wastewater samples.

The Dorhmann DX-20 system was modified (Figure 2) by replacing the boat entry system with a teflon-lined silicone septum held in a ball and socket glass fitting. The oxygen reagent gas entered the system through a 16-gauge stainless steel needle piercing the septum, while the CO_2 reagent gas entered through the purge assembly as before. The instrument flow controllers were bypassed and auxiliary flow controllers placed in both gas lines, in order to allow both gases to flow at the same time (i.e., the DX-20 gas switching mechanism was bypassed). Gas flows of 300 and 100 mL/minute were used for CO_2 and O_2, respectively. The use of both gases were considered to be important since the organic solvent requires O_2 content in order to be combusted, whereas any bromine compounds would be converted to bromate (and not detected) if pure oxygen was used.

Solutions containing components of interest in either cyclohexane or hexadecane were injected at a rate of 1 μL/second into the furnace tube at a point approximately 6 inches from the septum end of the furnace tube using a 5 or 25-μL syringe with a 4-inch long, 26-gauge needle. The instrumental analysis parameters used were identical to those in U.S. EPA Method 450.1, except for the modifications described above.

DETERMINATION OF EOX IN SOLIDS

The development of a method for determining EOX in solids was considered to be necessary because of the need to isolate and analyze separately the suspended solids in wastewater samples. The approach selected was to extract the solid residue with a polar organic solvent, in order to extract both polar and nonpolar organic halides, and to analyze the solvent extract using the procedure described above. Direct introduction of solids into the instrument was not appropriate because a significant proportion of the inorganic halide was found to be transferred through the system in addition to the organic halides.

The EOX/solids procedure, described in detail in Appendix D, involves the following steps:

- One gram of wet solids was placed in a two-dram vial with one mL of reagent water and five mL of ethyl acetate.
- The mixture was vigorously shaken for a few seconds and then placed in a sonic bath (Branisonic Model 52) for 15 minutes.
- The mixture was allowed to settle for 10 minutes and the supernatant was transferred to a 15-mL conical centrifuge tube using a disposable pipette.

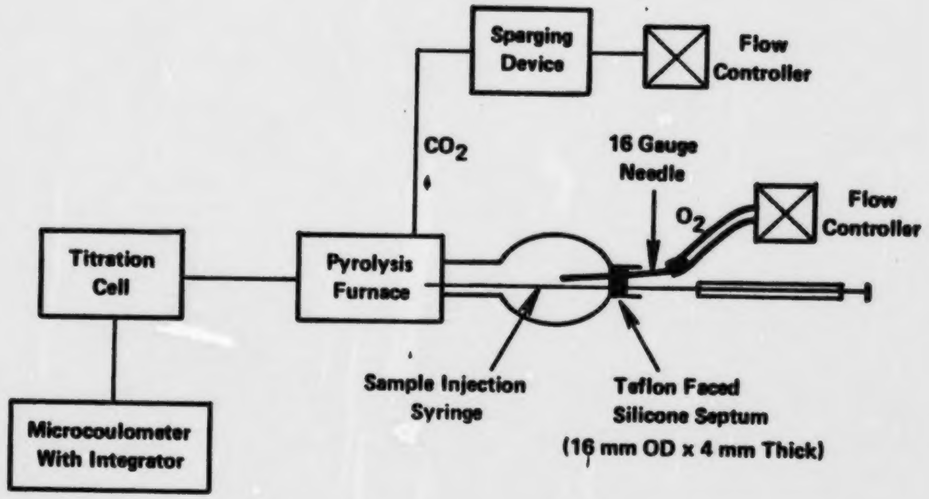
Sparging Device
Flow Controller
CO_2
16 Gauge Needle
O_2
Flow Controller
Titration Cell
Pyrolysis Furnace
Sample Injection Syringe
Teflon Faced Silicone Septum (16 mm OD x 4 mm Thick)
Microcoulometer With Integrator

Figure 2. System for determining organic halides in solvent extracts.

- The supernatant was centrifuged at approximately 1000x g for 5 minutes, to separate the solid and liquid phases, and the ethyl acetate layer was transferred to a two-dram vial having a teflon-lined cap.
- A 25-μL aliquot of the ethyl acetate layer was injected into the Dohrmann furnace as described above.

SECTION 6

RESULTS AND DISCUSSION

DETERMINATION OF ORGANIC HALIDES USING THE SBP APPROACH

As discussed previously, this analytical approach involved the following steps:

- Extraction of the organic halides into a suitable organic solvent
- Conversion of the organic halides to inorganic halide by addition of sodium biphenyl reagent to the organic extract
- Quenching of the reaction and neutralization of the solution by addition of a dilute nitric acid solution
- Determination of the inorganic halide in the neutralized solution using colorimetry.

The first SBP reagent, prepared in THF, was found to change from dark green to red over a period of two to three weeks, indicating that the SBP complex was decomposing. The second SBP reagent, prepared in glyme, using a somewhat simplified procedure was found to retain its dark green color for several months. The second reagent was used for all determinations reported herein.

Initial experiments centered on the evaluation of the sensitivity of ASTM Method D 512C (53). This procedure involves the addition of ferric ammonium sulfate and mercuric thiocyanate to an aqueous solution. Chloride ion reacts with the mercuric thiocyanate which ultimately reacts to form ferric thiocyanate which is determined colorimetrically at 463 nm, A typical calibration curve for chloride ion, using a 5-cm pathlength cell, is shown in Figure 3. The slope and intercept of the line were generally within ±10% when measured on successive days. As indicated by Figure 3, a chloride level of 10 µg/25 mL (0.4 µg/mL) was readily determined (significantly above the background level). Assuming a 1-liter sample volume and 25-mL volume after SBP reaction, this implies that a detection limit of approximately 10 µg/L can be achieved for water samples in an ideal situation.

In order to evaluate the overall analytical procedure two 100-mL aliquots of reagent water were spiked with 580 and 1750 µg/L of 1,2,4-trichlorobenzene

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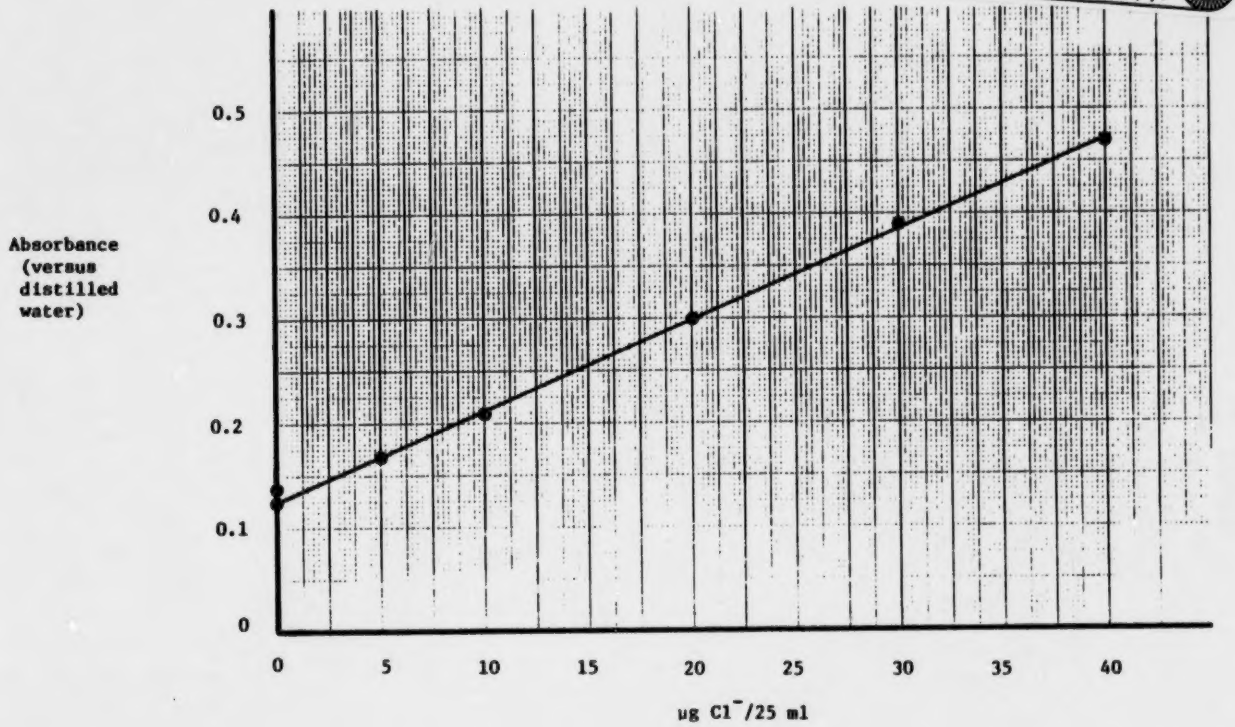

Figure 3. Calibration curve for colorimetric detection of chloride.

(equivalent to 340 and 1020 μg/L of Cl^-, respectively). The spiked water samples and two unspiked water samples were extracted with 1.5 mL of cyclohexane in a 100-mL volumetric flask. The small extraction volume was used to evaluate the possible use of the SBP procedure for volatile organic halides, which would be lost if a larger solvent volume was used and then concentrated.

Recoveries of 50% and 61% (after blank subtraction) were obtained for the 340-μg Cl/L and 1020-μg Cl/L. Blank levels were subsequently found to be unaffected by the addition of 500 mg/L of ferric chloride (as Cl^-) to the water sample prior to extraction. The unspiked samples both had apparent levels of 50 μg Cl/L. The background level was rather large and would require substantial reduction and/or precise control in order to achieve sufficient sensitivity. Extraction of a larger volume of water (e.g., 1 liter instead of 100 mL) would result in a proportionally lower detection limit. Such an approach could be employed for semivolatile, but not volatile, organic halides because of losses during the solvent evaporation step.

At this point in the study a decision was made to discontinue efforts on the SBP approach, in favor of the oxidation/microcoulometric titration approach. The latter approach appeared to be more sensitive and simpler to conduct. However, the SBP approach does appear to be viable and may be advantageous in certain situations (e.g., in laboratories where a microcoulometric system is not available and the sample load does not justify purchasing the device).

The use of ion selective electrodes (ISE) in place of the ASTM D 512C for Cl^- determination may also prove advantageous in some cases. A literature review indicated that detection limits for chloride are similar to, and in some cases better than, the colorimetric procedure, although the response for bromide is often much greater than for Cl^-, leading to ambiguous results using ISE.

EVALUATION OF METHOD FOR POX IN WATER USING THE MICROCOULOMETRIC TITRATION APPROACH

The Dohrmann DX-20 system (Figure 1) was found to be easily assembled and relatively simple to operate. Reagent water obtained from a Milli-Q water purification system was found to contain unacceptable levels of POX. Therefore, all experiments were conducted using Milli-Q water which had been passed through a charcoal column just prior to use. Initial experiments were performed to evaluate the accuracy and reproducibility of the instrument at various concentration levels. Chloroform, bromoform, 1,2-dichloroethane, and 1,2-dibromoethane were evaluated at various levels and the data obtained are shown in Tables 4-7.

Recoveries for chloroform and 1,2-dichloroethane were greater than 75% at 500 μg/L and above; however, recovery for chloroform was only 50% at 100 μg/L and was quite variable. The data shown in Tables 4 and 8 demonstrate an increasing recovery with increasing spike level for chloroform. The instrument manual for the DX-20 indicates that 95% recovery of chloroform should be obtained at the 100 μg/L level. Recovery of bromoform (Table 5)

TABLE 4. POX ANALYSIS OF REAGENT WATER SAMPLES SPIKED WITH CHLOROFORM USING DOHRMANN DX-20 SYSTEM

Compound Spike Level (μg/L)	Spike[a] Level (μg Cl/L)	Spike[a] Level (μmole Cl/L)	Amount Recovered (μg/L as Cl)	Mean and Standard Deviation (μg/L as Cl)	Amount Recovered (μmole Cl/L)	Recovery (%)[b]
10,000	8910	251	9,070 8,370 8,170	8,540 ± 470	241	95.9
5,000	4450	126	4,430 4,270 3,820	4,170 ± 320	118	93.6
1,000	891	25.1	730 737 699	722 ± 20	20.4	81.0
500	445	12.6	365 325 330	340 ± 22	9.59	76.3
100	89	2.5	71 27 36	45 ± 23	1.3	51

(a) Calculated amount = chloride mole fraction x chloroform concentration (in μg/L or μmole/L).

(b) Percent Recovery (% Cl^-) = detected amount (μmole Cl^-/L)/spike level (μmole Cl^-/L) x 100%.

TABLE 5. POX ANALYSIS OF REAGENT WATER SAMPLES SPIKED WITH BROMOFORM USING DOHRMANN DX-20 SYSTEM

Compound Spike Level (μg/L)	Spike[a] Level (μg Br/L)	Spike[a] Level (μmole Br/L)	Amount Recovered (μg/L as Cl)	Mean and Standard Deviation (μg/L as Cl)	Amount Recovered (μmole Br/L)[b]	Recovery (%)[c]
10,000	9,480	119	3,110 3,180 3,290	3,190 ± 90	90.0	75.8
5,000	4,740	59.4	1,630 1,610 1,630	1,620 ± 10	45.7	77.0
1,000	948	11.9	212 304 297	271 ± 51	7.64	64.4
500	474	5.94	113 159 108	127 ± 28	3.58	60.4
100	95	1.2	16 47 30	31 ± 16	0.87	73.7
50	47	0.59	40 19 7	22 ± 17	0.62	105

(a) Spike level = bromide mole fraction x bromoform concentration (in μg/L or μmole/L).

(b) $\mu\text{mole/L as Br} = \frac{\mu\text{g/L as Cl}}{35.5}$.

(c) Percent recovery (% Br^-) = amount recovered (μmole Br^-/L(/ spike level (μmole Br^-/L) x 100%.

TABLE 6. POX ANALYSIS OF REAGENT WATER SAMPLES SPIKED WITH 1,2-DICHLOROETHANE USING DOHRMANN DX-20 SYSTEM

Compound Spike Level (μg/L)	Spike[(a)] Level (μg Cl/L)	Spike[(a)] Level (μmole Cl/L)	Amount Recovered (μg/L as Cl)	Mean and Standard Deviation (μg/L)	Amount Recovered[(b)] (μmole Cl/L)	Recovery (%) (c)
10,000	7,170	202	6,230 6,120 6,190	6,180 ± 60	174	86.3
7,500	5,370	152	4,540 4,280 4,470	4,430 ± 130	125	82.4
5,000	3,580	101	3,090 3,060 3,030	3,060 ± 30	86.3	85.4
2,500	1,790	50.5	1,490 1,490 1,460	1,480 ± 20	41.7	82.6
2,000	1,430	40.4	1,230 1,160 1,160	1,180 ± 40	33.3	82.3
1,000	717	20.2	587 581 589	586 ± 4	16.5	81,8
500	358	10.1	288 284 280	± 284	8.01	79.3

(a) Spike level = chloride mole fraction x 1,2-dichloroethane concentration (in μg/L or μmole/L).

(b) $\mu\text{mole/L as Cl} = \frac{\mu\text{g/L as Cl}}{35.5}$.

(c) Percent recovery (% Cl^-) = Amount recovered (μmole Cl^-/L)/spike level (μmole Cl^-/L).

TABLE 7. POX ANALYSIS OF REAGENT WATER SAMPLES SPIKED WITH 1,2-DIBROMOETHANE USING DOHRMANN DX-20 SYSTEM

Compound Spike Level (μg/L)	Spike[(a)] Level (μg Br/L)	Spike[(a)] Level (μmole Br/L)	Amount Recovered (μg/L as Cl)	Mean and Standard Deviation (μg/L)	Amount Recovered[(b)] (μmole Br/L)	Recovery (%)[(c)]
10,000	8,510	106	1,930 1,920 1,960	1,940 ± 14	54.6	52
1,000	851	10.6	139 141 137	139 ± 2	3.9	37
500	425	5.3	63 75 69	69 ± 5	1.9	36
100	85	1.06	29 32 26	29 ± 3	0.82	77

(a) Spike level = bromide mole fraction x 1,2-dibromoethane concentration (in μg/L or μmole/L).

(b) μmole/L as Br = $\frac{\mu g/L \text{ as Cl}}{35.5}$.

(c) Percent detected (% Br^-) = amount recovered (μmole Br^-/L)/spike level (μmole Br^-/L) x 100%.

TABLE 8. POX ANALYSIS OF REAGENT WATER SAMPLES SPIKED WITH VARIOUS AMOUNTS OF CHLOROFORM USING THE DOHRMANN DX-20 SYSTEM

Spike Level (µg/L)	Spike Level (µg/L as Cl)	Amount Found, (µg/L as Cl)							
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average	Standard Deviation	Percent Recovery
0		0	1	0	0	0	-	-	
20	18	12	8	6	7	8	8	2	44
50	44	23	18	20	10	12	17	5	39
100	89	48	62	47	50	38	49	9	55
250	220	140	160	130	110	140	140	18	64
500	445	290	280	290	290	320	290	14	65

was approximately 60-75% at 100 µg/L and above. Although the apparent recovery of bromoform at 50 µg/L was 105%, the high variability in the measurement indicates that this recovery value is not precisely known. The recovery for 1,2-dibromoethane (Table 7) was 35-50% at all levels except the lowest level (100 µg/L) where a recovery of 77% was obtained. Excellent precision (less than ± 10% RSD) was obtained at all spike levels for 1,2-dibromoethane.

Because chloroform recovery was less than anticipated at the 100 µg/L, a more detailed study of the recovery of this compound at low spike levels was conducted. The results for this experiment, shown in Table 8, indicated that chloroform recovery was approximately 40-50% at spike levels less than 100 µg/L.

The instrument was inspected for operational problems such as leaks in the purge system, drift, and improper cell calibration. No such problems were found and frequent checks of the titration cell calibration (by injection of 5 µg of inorganic chloride directly into the cell) gave values within ± 2% of that expected.

Although the recovery of chloroform at low spike levels was less than expected, 80-100% recoveries were obtained at 1000 µg/L and above. In order to obtain comparative data on the recoveries of other POX compounds of interest, these compounds were analyzed at the 1000 µg/L level. A summary of the recovery data obtained are given in Table 9. In general, recoveries were 75% or greater for olefinic and aliphatic chlorine-containing compounds. However, recoveries for chloroaromatics and bromine-containing compounds were poorer, at approximately 50%. Relative standard deviations were 10% or less in all cases, indicating that the system was operating with good precision, in spite of the low recoveries obtained. The low recoveries did not appear to be related to incomplete purging since the cell output was found to return to background before the end of the 10-minute purge cycle in all cases.

A possible explanation for the low recovery of certain compounds is incomplete conversion to HCl or HBr (HX). The low recovery of chloroaromatics might be explained by their lower hydrogen content (required for conversion to HX).

Although the recovery of POX through the system was less than anticipated, the performance was considered to be adequate for evaluation of the performance of the POX surrogate method for various wastewater samples. A detailed writeup of the POX surrogate method is given in Appendix A. The samples for which the method was evaluated are listed below:

- Columbus, Ohio, tap water
- Final sewage effluent from the Columbus, Ohio, publicly owned treatment works (POTW)
- A final effluent from a plant producing aniline and related compounds

TABLE 9. OVERALL RECOVERY FOR VARIOUS POX COMPOUNDS SPIKED AT 1000 μg/L INTO REAGENT WATER USING THE DORHMANN DX-20 SYSTEM.

Compound	Recovery,%
Methylene chloride	87 ± 4(a)
Chloroform	81 ± 3(b)
Trans 1,2-Dichloroethylene	106 ± 0.2
1,1-Dichloroethane	94 ± 3
1,1-Dichloroethylene	78 ± 2
1,1,2,2-Tetrachloroethane	88 ± 6
Tetrachloroethylene	86 ± 0.6
Carbon Tetrachloride	86 ± 1
1,1,2-Trichloroethane	76 ± 8
1,2-Dichloropropane	76 ± 2
Trichlorofluoromethane	79 ± 7
Trichloroethylene	76 ± 2
1,1,1-Trichloroethane	68 ± 10
1,2-Dichloroethane	70 ± 4
1,3-Dichloropropene	60 ± 4
Chlorobenzene	48 ± 7
1,2-Dichlorobenzene	65 ± 5
1,3-Dichlorobenzene	51 ± 7
1,4-Dichlorobenzene	61 ± 7
Bromodichloromethane	47 ± 9
Bromoform	64 ± 8

(a) Relative standard deviation (%).
(b) Data from Table 4.

- Two final effluent samples from separate sites producing chlorinated hydrocarbon solvents.
- An aqueous leachate from a spent $FeCl_2$ catalyst solid waste (chloroethylene manufacturing).
- A wastewater from a chemical manufacturing plant in which methylene chloride is used as a solvent (designated Wastewater #3).

The POTW wastewater was found to foam somewhat, although the use of a 5-mL rather than a 10-mL aliquot was found to prevent the water from foaming into the furnace tube. Consequently 5-mL volumes were used for all of the wastewater analyses. Both the aniline wastewater and the solid-waste leachate had to be diluted because of the high levels of POX present.

Results of analysis for the various water samples using the surrogate method are given in Table 10. Results of U.S. EPA Method 624 (GC/MS) analysis for the various samples are given in Tables 11-17. Table 18 summarizes the results obtained for the unspiked wastewater samples for both the surrogate POX method and Method 624. Since many of the samples were only analyzed once by Method 624, some caution must be exercised in interpreting the degree of correlation between Method 624 and the surrogate method for those samples.

Tap water was found to contain chloroform as the predominant POX component (24 µg/L), as shown in Table 11. Since chloroform recovery at this level has been 50-60%, this effect probably is responsible for the lower value for the surrogate method analysis compared to the Method 624 analysis of this sample (20 versus 24 µg/L).

The POTW sewage sample contained 1,2-dichloroethylene as the predominant POX component, as shown in Table 12. The somewhat higher value obtained using the surrogate method compared to Method 624 (68 versus 37 µg/L) may be due to the presence of other POX compounds which are not detected by the GC/MS purge and trap system. However, since the GC/MS data were obtained for only a single sample aliquot, extensive interpretation of this difference is not possible.

Chlorinated Hydrocarbon Wastewater No. 1 contained a variety of chloroethylenes and ethanes at similar levels (Table 13), whereas Chlorinated Hydrocarbon Wastewater No. 2 contained predominantly 1,2-dichloropropane (Table 14). The GC/MS and surrogate results for the first wastewater were significantly different (27 versus 114 µg/L) whereas excellent agreement (30 versus 32 µg/L) was obtained for the second wastewater. A possible explanation for these results is that in cases where a large number of low-level components are quantified, the GC/MS POX results will be more inaccurate (because of additive errors) than in cases where a single component is present (as for Wastewater No. 2). In other words, the POX approach determines all components as a lumped sum and hence a greater signal will be achieved in such cases than for GC/MS or other chromatographic techniques where each component is determined individually.

TABLE 10. POX DATA FOR VARIOUS WATER SAMPLES USING THE SURROGATE METHOD

Sample	Spike Component	Spike Level (μg/L as Cl^-)	Amount Found (μg/L as Cl^-) Rep 1	Rep 2	Rep 3	Average	SD	Percent Recovery
TAP Water	--	0	19	22	19	20	2	--
POTW Sewage	--	0	75	67	62	68	6	--
POTW Sewage	Chloroform	29	99	109	107	105	5	128
Chlorinated Hydrocarbon Wastewater No. 1	--	0	117	137	90	114	23	--
Chlorinated Hydrocarbon Wastewater No. 1	Chloroform	460	510	440	460	470	31	77
Chlorinated Hydrocarbon Wastewater No. 2	--	0	32	34	29	32	3	--
Chlorinated Hydrocarbon Wastewater No. 2	Chloroform	1500	810	750	800	780	30	50
Chlorinated Hydrocarbon Wastewater No. 2	Chloroform	4500	4400	3500	3700	3900	520	87
Solid Waste Leachate[(a)]	--	0	172	173	169	171	2	--
Solid Waste Leachate[(a)]	1,1-Dichloroethane	200	250	220	--	235	--	33
Solid Waste Leachate[(a)]	1,1-Dichloroethane	800	490	490	520	500	12	44
Aniline Wastewater[(b)]	--	0	15500	16100	15400	15700	360	--
Aniline Wastewater[(b)]	Chloroform	15000	38200	38100	38200	38200	50	145
Aniline Wastewater[(b)]	Chloroform	45000	56900	56400	57200	56800	370	90
Wastewater No. 3	--	0	470	510	550	510	40	--
Wastewater No. 3	Methylene chloride	800	1170	930	1000	1030	120	65

(a) Diluted 200:1 prior to analysis. Values are mg/L for the undiluted sample.
(b) Diluted 10:1 prior to analysis. Values are for undiluted sample.

TABLE 11. RESULTS FOR U.S. EPA METHOD 624 ANALYSIS OF BATTELLE TAP WATER

Compound	Amount of Compound Found (μg/L)	Amount Found (μg/L as Cl⁻)
Chloroform	24.0	21
1,1,1-Trichloroethane	0.2	0.2
Bromodichloromethane	4.5	3.4
Dichloroacetonitrile	0.5	0.3
Trichloroethylene	0.1	0.1
Dibromochloromethane	3.0	1.2
	32.3	26.0

TABLE 12. RESULTS FOR U.S. EPA METHOD 624 ANALYSIS OF COLUMBUS POTW WASTEWATER

Compound	Amount of Compound Found (μg/L)	Amount Found (μg/L as Cl)
Vinyl chloride	1.4	0.8
Chloroethane	1.0	0.6
Methylene chloride	4.4	3.7
Trichlorofluoromethane	0.1	0.1
1,1-Dichloroethylene	0.3	0.2
1,1-Dichloroethane	2.4	1.7
1,2-Dichloroethylene	18.5	13.5
Chloroform	1.9	1.7
1,1,1-Trichloroethane	4.7	3.7
Carbon tetrachloride	1.0	0.9
Trichloroethylene	3.9	3.2
Tetrachloroethylene	7.1	6.1
Chlorobenzene	1.7	0.5
	48.4	37

TABLE 13. RESULTS FOR U.S. EPA METHOD 624 ANALYSIS OF CHLORINATED HYDROCARBON WASTEWATER NO. 1

Compound	Amount Found (μg/L)	Amount Found (μg/L as Cl)
Methylene chloride	1.3	1.1
1,1-Dichloroethylene	0.7	0.5
1,1-Dichloroethane	0.3	0.2
1,2-Dichloroethylene	0.6	0.4
Chloroform	2.5	2.1
1,2-Dichloroethane	10.7	7.6
Trichloroethylene	6.6	5.3
1,1,2-Trichloroethane	6.5	5.3
Tetrachloroethylene	4.9	4.2
Total	34	27

TABLE 14. RESULTS FOR U.S. EPA METHOD 624 ANALYSIS OF CHLORINATED HYDROCARBON WASTEWATER NO. 2

Compound	Amount Found (μg/L)	Amount Found (μg/L as Cl)
Methylene chloride	3.8	3.2
Chloroform	0.3	0.3
1,2-Dichloroethane	3.6	2.6
1,2-Dichloropropane	37	23
Trichloroethylene	0.2	0.2
Tetrachloroethylene	0.6	0.5
Total	46	30

TABLE 15. RESULTS FOR U.S. EPA METHOD 624 ANALYSIS OF LEACHATE FROM FERROUS CHLORIDE CATALYST WASTE SAMPLE

Compound	Amount Found (µg/L)[a] Rep 1	Rep 2	Rep 3	Average	SD	Amount Found (µg/L as Cl)
Chloroform	0.7	0.8	0.9	0.8	0.1	0.7
1,1-Dichloroethane	260	260	250	260	11	180
Methylene chloride	1.3	3.3	3.7	2.8	1.3	2.3
1,2-Trans-dichloroethylene	19	17	17	18	1.0	13
1,1,1-Trichloroethane	4.8	4.9	5.3	5.0	0.3	4.0
1,1,2-Trichloroethane	1.2	1.1	1.8	1.4	0.4	1.1
TOTAL						200 ± 9[b]

[a] Sample diluted 1000:1 before analysis. Results shown are for original sample in terms of mg/L (ppm).

[b] Standard deviation calculated from the total amounts (as Cl) found for each replicate.

TABLE 16. RESULTS FOR U.S. EPA METHOD 624 ANALYSIS OF ANILINE WASTEWATER

Compound	Amount of Compound Found (μg/L)	Amount Found (μg Cl^-/L)
Chloroethane	19	10
Methylene chloride	1100	920
Trichlorofluoromethane	92	71
1,2-Dichloroethylene	280	200
Chloroform	12300	11000
1,2-Dichloroethane	9	6
1,1,1-Trichloroethane	150	119
Carbon tetrachloride	1300	1200
1,1,2,Tetrachloroethane	40	34
Dichloropropene	55	35
Chlorobenzene	56500	17800
Dichlorocyclohexane	2	1
	71900	31400

TABLE 17. RESULTS FOR U.S. EPA METHOD 624 ANALYSIS OF WASTEWATER NO. 3

Compound	Amount Found (μg/L)			Amount found (μg/L as Cl)
	Rep 1	Rep 2	Average	
Methylene Chloride	700	660	680	570
1,1-Dichloroethene	84	77	80	58
1,2-Dichloroethane	23	21	22	16
1,1,2-Trichloroethane	120	120	120	97
TOTAL			900	740

TABLE 18. COMPARISON OF U.S. EPA METHOD 624 AND SURROGATE POX DATA FOR VARIOUS WATER SAMPLES

Sample	Amount Found (µg/L as Cl) Method 624	Amount Found (µg/L as Cl) Surrogate Method
Top water	26	20 ± 2
POTW Sewage	37	68 ± 6
Chlorinated hydrocarbon		
Wastewater No. 1	27	114 ± 23
Wastewater No. 2	30	32 ± 3
Solid waste leachate	200 ± 9(a)	171 ± 2(a)
Aniline wastewater	31,400	15,700 ± 360
Wastewater No. 3	740(b)	510 ± 40

(a) mg/L. Triplicate analysis. All other data represent single analyses.

(b) Duplicate analysis.

Excellent agreement was obtained between the Method 624 (Table 15) and surrogate results (200 ± 9 versus 171 ± 2 mg/L) for the solid-waste leachate sample although the recovery efficiency for 1,1-dichloroethane, the major component in this sample, was only 40%. The reason for obtaining good agreement between the methods, but not quantitatively recovering the spiked component is not clear. Replicate GC/MS as well as surrogate method data were acquired for this sample and relative standard deviations of less than 5% were obtained for both methods. Because of the very high level of POX this sample was diluted 200:1 prior to analysis.

Aniline wastewater was found to contain chlorobenzene as the major halogenated organic compound (Table 16), with a significant level of chloroform also being present. The surrogate method gave a value of 15,700 μg/L compared to the Method 624 value of 31,400 μg/L. This result is probably due to the low recovery of chlorobenzene in the POX system (Table 9). Method 624 compensates for losses due to poor purging efficiency and other factors by introducing internal standards into each sample and by instrument calibration using spiked water samples whereas the surrogate method uses an absolute calibration scheme (i.e., direct injection of inorganic halide into the titration cell). Therefore, any loss due to incomplete conversion to HX or other causes will cause an inaccuracy in the results.

Wastewater No. 3 contained methylene chloride as the only major halogenated organic (Table 17). The surrogate POX and Method 624 values were 510 and 740 μg/L, respectively. These data seem reasonable, on the basis that a 65% recovery of methylene chloride was obtained for this sample using the POX surrogate method. Again these data indicate that in a situation where one major species is present the data for the two methods agree quite well.

The precision of the POX method, given in Table 10, was excellent (5-10%) in most instances. Recoveries generally were comparable to those obtained for reagent water, although for the solid waste leachate recovery of 1,1-dichloroethane was only 35-45%. Several attempts were made to improve the purging efficiency of dichloroethane. Decreasing the CO_2 flow to 150 mL/min (to increase residence time in the furnace), purging with O_2 rather than CO_2, and sparging at 30° and 60°C all gave identical results to those given in Table 3 (for 1,1-dichloroethane in reagent water).

In order to assess the low limit of detection of the POX surrogate methods, several compounds were run according to the U.S. EPA/EMSL protocol for determining method detection limits (MDL). This protocol is described in Appendix B. The data obtained in this experiment are shown in Table 19. Although the recoveries obtained for most of the compounds were similar to the recoveries previously obtained, chloroform unexpectedly was quantitatively recovered in this experiment. MDLs at 2-5 μg/L were obtained in all cases except bromoform, which was not recovered at the 30-μg/L level. However, chlorobenzene gave an artificially low MDL value because of the low, but relatively precise, recovery. As noted in Table 19, the practical MDL for chlorobenzene is probably greater than the calculated value since the 8-μg/L spike gave a barely detectable signal.

TABLE 19. METHOD DETECTION LIMIT DATA FOR POX ANALYSIS OF SELECTED COMPOUNDS

Compound	Spike Level (µg/L)	Spike Level As Cl (µg/L)	Amount of POX Found (µg/L as Cl)										Recovery
			Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	AV	SD	MDL(1)	
Chloroform	12.5	11	12	12	13	9	11	10	12	11	1.4	4.5	100
Trichloroethene	14	10	6	6	5	5	6	7	6	6	0.7	2.2	60
Tetrachloroethene	14	10	6	6	5	6	6	5	4	5	1.0	3.2	50
Chlorobenzene	25	8	3	2	3	3	3	4	3	3	0.6	2.0(2)	38
Bromoform	30	13	ND	ND	ND	ND	ND	ND	ND				<10

(1) Calculated using EMSL Protocol (54).

(2) Practical MDL probably is greater than the calculated value, because of low recovery.

(3) ND = Not Detected. Recovery for bromoform at 300 µg/L (130 µg/L as Cl) was 48% and 49% for duplicate analyses.

Bromoform gave no detectable signal (∿10% recovery) at the 30-μg/L (13 μg/L as Cl^-) level. Subsequent duplicate analysis at 300 μg/L gave 48% and 49% recoveries for bromoform, indicating that the recovery decreases substantially as the concentration decreases. The detection limit for bromoform appears to be 100 μg/L (44 μg/L as Cl^-) based on data obtained previously (Table 5). This result indicates that the surrogate POX method is not suitable for determining bromoform in most practical situations, since the bromoform level rarely exceeds 100 μg/L in relevant water samples.

Based on the results obtained of this study it appears that the surrogate POX method can be used as an indicator of organic halide pollution in a variety of water types. However, several limitations of the method must be recognized. First, the recovery of POX components was not found to be 95% or greater, as implied in the instrument manual. Although chloroform recovery was quantitative in one experiment, recoveries of 60-90% (depending on level) were normally observed. Secondly, the recovery of brominated species is not quantitative and, at least in the case of bromoform, levels of less than 100 μg/L cannot be quantified.

Nevertheless, the results obtained for a variety of water samples using both the surrogate POX method and U.S. EPA Method 624 agreed within a factor of two in most cases. The POX value obtained on an uncharacterized water sample will vary substantially depending on the properties of compounds present (e.g., bromine versus chlorine, percent halogen, purging efficiency, etc.). In view of these uncontrollable factors, the agreement between GC/MS and the surrogate POX method is considered to be satisfactory. However, the system performance may be capable of yielding improved recoveries if such parameters as purge gas, purge rate, furnace temperature, etc., are systematically evaluated. Such evaluations were beyond the scope of the study reported herein. Recognizing the inadequacies of the POX method for certain compounds, the overall results indicate that POX is acceptable as a semiquantitative indicator of pollutant level.

EVALUATION OF U.S. EPA METHOD 450.1 FOR THE DETERMINATION OF TOX IN WASTEWATER

The objective of this phase of the program was to evaluate U.S. EPA Method 450.1, which had originally been developed for drinking water, as a method for determining TOX in wastewater samples. Method 450.1 is described in detail in Appendix C. Two modifications to the method were found to be useful, as described below. First, the granular activated charcoal (GAC) columns were washed with methanol, water, and then nitrate solution prior to sample adsorption, in order to remove adsorbed organic halides. Secondly, the nitrate rinse volume, after adsorption, was increased from 2 mL to 5 mL in order to more completely remove inorganic halide. Since the washing step is conducted with the two columns in series, any loss of components due to desorption from the first GAC column would be evidenced by a high backup GAC organic halide level. Since this result was not observed, the 5-mL volume of nitrate appears to have no effect on recovery of TOX components.

Initially, the method was evaluated for tap water analysis on two different days, one week apart. The data obtained in this experiment are shown in Table 20. Reagent water was prepurified by passage through a large GAC column as described in the POX section. The blank GAC data were similar on two different days, as were the tap water data. Blank GAC values of 0.7 - 1 µg/column were generally obtained throughout the study, as long as the GAC was stored in a tightly sealed screw-capped vial in a desiccator. However, at one point the capped GAC bottle was accidently left in the laboratory environment (not in the desiccator) for 2-3 weeks and a very high GAC blank was obtained. Precision for both the tap water and a surface water sample was excellent, and very low levels of organic halide were found in the backup columns, indicating that breakthrough was not a problem.

A series of experiments were then conducted to investigate the extent to which inorganic halide interferred in the method. In the first experiment, a reagent water sample containing 10 g/L of NaCl were analyzed unspiked and spiked with 1000 µg/L of 1,2,4-trichlorobenzene. The data for this experiment, given in Table 21, indicate that this level of inorganic halide does not interfere in the method and that trichlorobenzene is quantitatively recovered. Similar data obtained using other inorganic halide salts are given in Table 22. Only $FeCl_2$ and $MnCl_2$ gave substantial interferences at the 500-mg/L level. In all cases where some elevation was noted, the values obtained were highly variable indicating that incomplete rinsing was the problem. These data were collected using the original 2-mL nitrate wash volume. In spite of this fact, the levels of interference indicated, even in the worst case, were minimal and of no practical concern.

Because of the presence of suspended solids in certain wastewaters an alternate approach to the GAC column approach, namely the GAC slurry approach, was investigated. However, the complete removal of inorganic halide was found to be extremely difficult, compared to the GAC column approach, wherein the column can be efficiently washed with a small volume of nitrate solution. Consequently, the decision was made to separate out the suspended solids by centrifugation and to analyze the residue by a solvent extraction approach described later in this report.

The TOX method, U.S. EPA Method 450.1 modified as described above, was applied to a variety of water samples, both spiked and unspiked. The results are summarized in Table 23. The water types evaluated included:

(1) Reagent water

(2) An industrial wastewater from an aniline manufacturing facility

(3) An industrial wastewater from a chlorinated hydrocarbon manufacturing facility

(4) An industrial wastewater from a second chlorinated hydrocarbon manufacturing facility

(5) An aqueous leachate from a ferrous chloride spent catalyst waste sample

(6) POTW sewage from the Columbus, Ohio plant.

TABLE 20. RESULTS OF TOX ANALYSIS OF COLUMBUS TAP WATER SAMPLES

	Amount of Cl Detected in 100-ml Aliquot, μg					
Sample	Rep 1	Rep 2	Rep 3	Average	Standard Deviation	μg TOX/L [a]
Day 1 [b]						
GAC Blank	1.12	1.08	0.87	1.02	0.13	
Tap Water	18.4 (1.3)[c]	17.6 (1.3)	18.3 (1.7)	18.1 (1.4)	0.45 (0.21)	175
Day 2 [b]						
GAC Blank	0.76	0.73	0.79	0.76	0.03	
Tap Water	20.0 (1.6)	20.4 (1.5)	19.7 (1.5)	20.0 (1.5)	0.33 (0.04)	200
GAC Blank	0.96	0.75	0.72	0.81	0.13	
Surface Water (Olentangy River)	10.4 (1.4)	9.1 (1.6)	9.5 (1.5)	9.7 (1.5)	0.63 (0.08)	95

a. Corrected for blank value.

b. Day 1 and day 2 were one week apart.

C. Numbers in parentheses are levels in backup GAC columns.

TABLE 21. RESULTS OF TOX ANALYSIS OF SODIUM CHLORIDE(a,b)

Sample	Spike Level µg/Cl	Amount Found µg Cl/sample				Percent Recovery
		Rep 1	Rep 2	Rep 3	Ave.	
10 g/L NaCl	0	0.31	1.12	--	0.71	NA
10 g/L NaCl spiked with trichlorobenzene	100	86.6	91.3	97.0	91.6	92

(a) 100 mL samples

(b) GAC columns washed with 5 mL of 0.08 N KNO_3 solutions

NA Not applicable

TABLE 22. RESULTS OF TOX ANALYSIS OF METAL CHLORIDE SOLUTIONS

	Amount of Cl^- Detected, μg, for Given 100 mL Sample		
Salt	Blank	50 mg/L Salt Solution	500 mg/L Salt Solution
$CuCl_2$	0.84 ±0.06[a]	1.34 ±0.18	2.91 ±0.22
$ZnCl_2$	0.86 ±0.12	1.22 ±0.28	1.16 ±0.13
$FeCl_2$	0.86 ±0.08	2.71 ±1.56	6.45(b) ±5.0
$MnCl_2$	0.92 ±0.06	1.65 ±1.18	4.40(c) ±7
$NiCl_2$	1.01 ±0.08	2.28 ±0.78	1.38 ±0.55

(a) Mean ± standard deviation for three replicate determinations. Two milliliters of nitrate was used in all cases.

(b) Three individual values were 9.16, 7.4, and 2.4 μg of Cl^-.

(c) Three individual values were 11.2, 0.95, and 1.23 μg of Cl^-.

TABLE 23. TOX DETERMINATION IN WATER SAMPLES

Sample	Date of TOX Determination	POX µg/L as Cl^-	Extractable OX µg/L as Cl^- (a)	Spike Level µg/L as Cl^- (b)	Amount TOX Found µg as Cl^- in 100 mL Aliquot						Av TOX µg/L as Cl^- (c)	SD	Percent Recovery
					Rep 1		Rep 2		Rep 3				
					Col 1	Col 2	Col 1	Col 2	Col 1	Col 2			
Blank GAC	4/13	--	--	--	0.89	--	0.97	--	0.99	--	--	--	--
	4/23	--	--	--	0.72	--	0.85	--	0.81	--	--	--	--
	6/19	--	--	--	0.98	--	0.88	--	0.93	--	--	--	--
	7/9	--	--	--	0.92	--	0.90	--	0.93	--	--	--	--
	2/27	--	--	--	0.81	--	0.76	--	0.85	--	--	--	--
Reagent Water	2/27	--	--	0	1.33	0.88	1.15	0.98	1.20	1.01	5	1	--
	2/27	--	--	29	3.00	1.27	3.75	0.92	3.52	1.20	26	4	71
Aniline Wastewater[d]	4/13	17,000	600	0	4.74	3.63	4.97	3.82	4.32	3.45	12,800	1,000	--
	4/13	17,000	600	8,800	9.28	4.14	8.79	4.18	9.73	3.96	22,900	650	114
	4/13	17,000	600	26,000	17.2	4.36	17.7	4.23	17.1	4.31	39,500	440	102
Chlorinated Hydrocarbon Wastewater #1[e]	4/23	114	9	0	14.1	1.45	12.9	1.37	13.35	1.40	1,330	65	--
	4/23	114	9	1,500	28.1	1.76	27.8	1.82	27.98	1.80	2,800	20	98
	4/23	114	9	4,500	53.8	1.85	54.4	1.70	56.4	1.81	5,480	110	92
Chlorinated Hydrocarbon Wastewater #2[f]	6/19	32	8	0	9.26	1.61	7.82	1.50	8.38	1.90	3,330	420	--
	6/19	32	8	4,000	16.7	1.71	15.9	1.64	16.7	1.78	6,480	380	79
	6/19	32	8	12,000	35.9	1.65	34.9	1.56	36.2	1.69	14,200	360	91
Solid Waste Leachate[g]	7/9	43,000	2400[h]	0	39.9	2.98	39.1	3.54	37.5	3.38	80,500	2,400	--
	7/9	43,000	2400	80,000	100	1.33	80.6	1.91	85.3	4.28	168,000	14,000	110
	7/9	43,000	2400	240,000	170	7.97	155	8.24	135	9.89	320,000	64,000	100
POTW Sewage	2/27	17	--	0	8.57	1.98	7.84	1.81	7.42	1.76	78	7	--
	2/27	17	--	29	10.6	0.94	11.2	1.36	10.9	1.49	105	4	93

(a) Determined using U.S. EPA Method 625 for unspiked aliquot unless otherwise specified.
(b) 1,2,4-Trichlorobenzene spiked.
(c) Calculated as specified in U.S. EPA Method 450.1 using the average GAC blank value for that day and correcting for sample dilution.

$$(\text{TOX } (\mu g/L \text{ as } Cl^-) = \frac{\text{TOX (Col 1)} + \text{TOX (Col 2)} - 2\ \text{TOX (Blank)}}{0.1\ \text{L (Sample Aliquot)}} \times \text{Dilution Factor}$$

(d) Diluted 200:1.
(e) Diluted 10:1.
(f) Diluted 20:1.
(g) Diluted 100:1.
(h) Determined by U.S. EPA Method 612 for unspiked aliquot using Hall detector.
SD = Standard Deviation.
GAC = Granular Activated Charcoal.

Water samples 2-5 (above) all contained between 5 and 10 grams per liter of inorganic halide. The samples were diluted to a level sufficient to ensure that no more than 50 μg of TOX was adsorbed on the GAC columns. The aniline wastewater was centrifuged for 5 minutes at 1000x g in order to remove suspended solids. One hundred milliliter aliquots (after dilution, if necessary) were analyzed in all cases.

In all cases, good recovery was obtained for the 1,2,4-trichlorobenzene spike. Generally, analytical precision was approximately 5-10% RSD. For all samples except the aniline wastewater, the backup GAC column contained relatively low amounts of TOX, indicating that good adsorption efficiency was being obtained and that dissolved inorganic halide was not contributing to the TOX value.

The aniline wastewater gave substantial breakthrough of TOX into the second GAC column, even after 200:1 dilution. Since most of the TOX value could be attributed to chlorobenzene, on the basis of the GC/MS results, chlorobenzene appeared to be breaking through the GAC, although trichlorobenzene was demonstrated to be efficiently recovered on the first GAC column.

To further clarify the aniline wastewater data, duplicate 100-mL aliquots of the wastewater were analyzed, unspiked and spiked with chlorobenzene. The data obtained in this experiment are shown in Table 24. A recovery of 64% was obtained for chlorobenzene in this experiment and all of the chlorobenzene was retained on the first GAC column. In fact, less TOX was present on the second GAC column when chlorobenzene was present than was observed for the unspiked sample. These data clearly show that chlorobenzene breakthrough is not the cause for the high level of TOX observed in the second GAC column for the unspiked sample. The cause of this phenomenon is still unclear, although the good agreement between the results for the unspiked wastewater reported here and those reported in Table 23, previously, indicates that the effect is reproducible.

All of the wastewater samples except the aniline wastewater gave substantially higher TOX values than were accounted for on the basis of POX and EOX values. This result seems to indicate that polar, nonextractable materials such as chlorinated humic acids are contributing to the TOX value. Inorganic halide does not appear to be a contributing factor since the second GAC column is relatively low in TOX. Inorganic halide would be expected to occlude in both GAC columns equally, since these salts are not efficiently adsorbed on GAC.

Extraction of the chlorinated hydrocarbon wastewater #2 with ethyl acetate at both neutral and low pH (pH 2) did not yield additional EOX content (determined by U.S. EPA Method 612 using a Hall detector) indicating that the TOX species present in the wastewater are highly polar.

In general, the TOX method appears to be well suited for wastewater analysis in view of the good precision and accuracy obtained in this study. However, the relatively high TOX values compared to EOX (as determined by U.S. EPA Method 625) tend to reduce the applicability of the method for determining trace quantities (10-100 μg/L) of industrial chlorinated

TABLE 24. TOX RESULTS FOR ANILINE WASTEWATER USING CHLOROBENZENE SPIKE

Chlorobenzene Spike Level		TOX on Given GAC Column (μg)				TOX as Cl^- μg/L[(a)]		Percent Recovery
		Rep 1		Rep 2				
μg/L	μg/L as Cl^-	Col 1	Col 2	Col 2	Col 2	Rep 1	Rep 2	
0	0	4.99	3.64	4.38	3.87	14,000	13,400	--
64,000	20,000	12.77	2.03	12.97	2.07	26,200	27,000	64

(a) Calculated as follows:

$$\text{TOX } (\mu g/L) = \frac{\text{TOX (Col 1) + TOX (Col 2) - 2 TOX (Blank)}}{\text{0.1L (Sample aliquot)}} \text{ x Dilution Factor (200)}$$

where TOX (Blank) is the GAC blank level, in this case 0.79 μg.

chemicals such as PCBs or chlorinated pesticides (i.e., correlation between EOX and carbon adsorbable OX is generally not very good). In many cases, it is conceivable that a solvent extractable TOX value (e.g., ether or ethyl acetate extraction of the wastewater followed by analysis of the extract using the DX-20) would be more relevant. On the other hand, the extraction approach will fail to determine many polar organic halides which might be of interest. Consequently, the selection of carbon adsorption as opposed to other isolation approaches, in effect, operationally defines the TOX parameter as "those organic halides which are adsorbed on GAC".

DETERMINATION OF EOX IN WATER

An approach for the determination of organic halides by solvent extraction was investigated, using the Dohrmann DX-20 system modified as described in the experimental section. In order to determine whether or not this approach would be successful in determining priority pollutant chlorinated hydrocarbons, each of the compounds of interest was injected individually into the system. Twenty-five μL of a 0.4-μg Cl/μL solution of each compound in 50:50 cyclohexane:hexadecane was injected. This experiment was repeated using a 5-μL injection volume. The results of this experiment are shown in Table 25. The results for the 25-μL injections are highly accurate whereas the results for 5-μL injections were uniformly greater than 100%. The difference in accuracy of the two injection volumes is well explained on the basis of sample evaporation from the syringe needle, and can be prevented using a solvent flush technique. After a 5-μL injection, 0.5 to 0.7 μL of needle volume was "missing" and presumed to be injected via needle evaporation; this corresponds to 10% to 14% additional sample. The 25-μL syringe was equipped with a needle of the same inside diameter as the 5-μL syringe, and the same amount of needle evaporation in this case would correspond to only 2.0% to 2.8% of additional sample injected. These data clearly demonstrate that the solvent extraction approach is feasible for the determination of priority pollutant semivolatile chlorinated hydrocarbons.

An experiment was conducted to determine the linear range of the Dohrmann response for 1,2,4-trichlorobenzene (TCB) when using solvent injection. A series of TCB standards ranging in concentration from 0.02 to 2-μg Cl/μL in cyclohexane were prepared. Five-μL and 25-μL volumes of each solution were injected into the Dohrmann system. The results for this experiment are given in Table 26.

The data in Table 26 demonstrate that the detection limits are similar for 5-μL and 25-μL injection volumes, since the background level increases with increasing injection volume. However, the data for 25-μL injections appear to be more accurate. The background level of 0.23-μg Cl/25-μL injection is equivalent to ∿10 μg/L in a water sample, assuming a 100-fold concentration factor. This value is in the range of the detection limit for the GAC method.

The solvent injection approach was applied to Columbus tap water, Columbus POTW sewage, and the aniline manufacturing wastewater. The method involved extraction of a 1-liter sample aliquot with 3 x 60 mL of cyclohexane,

TABLE 25. RESPONSE FOR CHLORINATED HYDROCARBONS INJECTED INTO THE DOHRMANN SYSTEM

	5-µl Injection			25-µl Injection		
Compound	Amount Expected (µg Cl^-/L)	Amount Found (µg Cl^-/L)	% Recovery	Amount Expected (µg Cl^-/L)	Amount Found (µg Cl^-/L)[b]	% Recovery
1,2,4-Trichlorobenzene	2.00	2.33 ± 0.07[a]	116	10.0	10.2	102
Hexachloroethane	2.00	2.44 ± 0.13	122	10.0	10.3	103
2-Chloronaphthalene	2.00	2.44 ± 0.16	122	10.0	10.3	103
Hexachlorobenzene	2.00	2.27 ± 0.04	114	10.0	10.0	100
1,2-Dichlorobenzene	2.00	2.41 ± 0.09	120	10.0	10.1	101
Hexachlorobutadiene	2.00	2.37 ± 0.06	118	10.0	9.6	96
1,3-Dichlorobenzene	2.00	2.23 ± 0.06	112	10.0	9.9	99
Hexachlorocyclopentadiene	2.00	2.38 ± 0.19	119	10.0	10.1	101
1.4-Dichlorobenzene	2.00	2.45 ± 0.14	122	10.0	9.7	97
Solvent Blank	0	0.03 ± 0.006	-	0	0.18	-

(a) Average and standard deviation for three determinations.

(b) Average for two determinations.

TABLE 26. RESPONSE FOR TCB INJECTED AT VARIOUS LEVELS INTO THE DOHRMANN TOX SYSTEM

Concentration µg Cl/µL	5-µL Injection			25-µL Injection		
	Amount Expected (µg Cl)	Amount Found (µg Cl)[a]	% Recovery[b]	Amount Expected (µg Cl)	Amount Found (µg Cl)[a]	% Recovery[b]
0	0	0.04	-	0	0.23	-
0.02	0.10	0.12	80	0.50	0.62	78
0.06	0.30	0.34	100	1.5	1.6	91
0.2	1.0	1.1	106	5.0	5.0	95
0.6	3.0	3.3	109	15.0	14.7	96
2.0	10.0	11.3	113	50.0	50.9	101

(a) Average of two determinations.

(b) Corrected for background level.

concentration of the extract to 1 mL using a Kuderna-Danish (KD) evaporator, and replicate injection of 5-µL and 25-µL aliquots of the extract into the Dohrmann system. The results for this experiment are shown in Table 27. The recoveries for the three water samples are quite good. Although slightly better recoveries are indicated by the 5-µL injection volumes, these values are probably high due to systematic error, as was demonstrated in the standard injection experiments described above. The high EOX level in the aniline wastewater is presumably due to incomplete removal (by evaporation) of chlorobenzene (the major POX component) during the solvent concentration step.

An experiment was conducted to determine if the U.S. EPA Method 612 (49) methylene chloride extraction scheme could be used in place of cyclohexane extraction. One-liter aliquots of spiked and unspiked distilled water were extracted using the Method 612 protocol (three times with 60-mL aliquot of methylene chloride). Following exchange into cyclohexane, as described in Method 612, the extract was exchanged by the addition of 0.5 mL of hexadecane and KD concentration to 1.0 mL. Values of 6- and 7-µg Cl/liter were obtained for duplicate analysis of the unspiked sample and the duplicate recovery determinations for the spiked sample were 74 and 75% (20-µg Cl/L TCB). These experiments indicate that the solvent injection approach will work well for the priority pollutant chlorinated hydrocarbons (i.e., a surrogate method for U.S. EPA Method 612). However, it would not be as useful as the GAC adsorption approach in determining total organic halogen (i.e., polar species will be isolated by GAC but not by solvent extraction).

DETERMINATION OF EOX IN SOLIDS

A method for determining EOX in solids was evaluated. This approach involved the use of ethyl acetate as an extraction solvent for isolating EOX components from solids and determination of EOX in the extract using the solvent injection/microcoulometric titration approach described above. The selection of ethyl acetate was based on the desire to have a polar, water-immiscible organic solvent which would be capable of extracting both polar and nonpolar organics, but would not dissolve inorganic halide. This method for EOX/solids analysis is presented in standard U.S. EPA format in Appendix D. Direct introduction of solid materials (e.g., sodium chloride) into the boat inlet resulted in significant transfer of inorganic halide through the system. Hence this approach is not useful for organic halide determination.

The EOX procedure was evaluated using the various solid samples described below:

(1) A garden soil which had been dried and passed through a 30-mesh sieve

(2) The wet solids (47% solids) isolated from an aniline manufacturing wastewater

TABLE 27. RESULTS FOR SOLVENT EXTRACTION OF WATER AND WASTEWATER USING THE DOHRMANN TOX SYSTEM

Sample	Spike Level µg Cl/L	5-µL Injection Amount Found µg Cl$^-$/L	5-µL Injection % Recovery	25-µL Injection Amount Found µg Cl$^-$/L	25-µL Injection % Recovery
Process Blank	0	6	-	5	-
Tap Water	0	16	-	10	-
Tap Water	200 (TCB)	200	92	150	70
POTW Sewage	0	6	-	6	-
POTW Sewage	100 (TCB)	100	94	86	80
Aniline Wastewater	0	2400	-	ND	ND
Aniline Wastewater	15,000 (TCB)	16,800	96	ND	ND

ND = Not determined.

(3) A wet solid waste (64% solids) which was obtained from a solid waste landfill

(4) A ferrous chloride spent catalyst waste (85% solids) from a chloroethylene manufacturing plant

(5) A drying bed solids waste (50% solids) from a chloroethylene manufacturing plant.

The solids were spiked with methanol stock solutions of trichlorobenzene, trichloroaniline, or trichlorophenol at various levels. No more than 50 µL of methanol per gram of wet solids were used in the spiking procedure in order to minimize the effect of the spiking process on the properties of the solid materials. The spiked materials were tumbled overnight in two-dram vials in order to ensure adequate equilibration of the solids with the spiked components. Further experimental details are provided in Section 5 of this report.

Results obtained for the various solids, spiked and nonspiked, are given in Table 28. Trichlorobenzene (TCB) was used as the spike compound in all cases, except for the "clean" soil where 2,4,6-trichloroaniline (TCA) and 2,4,6-trichlorophenol (TCP) recoveries were also determined.

The soil sample had a background level very close to that of the process blank (approximately 5 µg/g). Recovery of TCB was 58% when spiked at a level approximately equal to the background level whereas quantitative recovery was obtained for TCB at the higher spike level. Both TCA and TCP gave only 50-60% recovery at the higher spike level and TCP recovery was not improved substantially when the sample was adjusted to pH 2 with sulfuric acid prior to extraction. A second extraction of the TCA and TCP spiked samples did not recover any additional TCA or TCP. The losses of TCA and TCP are probably due to irreversible adsorption onto the soil, although additional work is required to verify this hypothesis.

Good precision and recovery of TCB were obtained for both the aniline solids and the "landfill" solid-waste sample. The aniline solids contained 830 µg/g of EOX. Since the water content of the wet solids was 53% and the water had previously been found to contain 11 µg/mL of TOX (by carbon adsorption), then the EOX content in the solid due to the water was approximately 6 µg/g and was negligible compared to the EOX in the solid.

The ferrous chloride catalyst waste contained a very high level (8400 µg/g) of EOX. Reextraction of the ethyl acetate extract with water did not reduce the EOX level substantially, indicating that inorganic chloride was not being extracted. A second extraction of the solid with ethyl acetate removed some additional EOX (approximately 30% compared with the first extraction). However, most of this material is probably due to carryover of the emulsified ethyl acetate/water interface from the first extraction, rather than additional organic halide being extracted.

The drying bed solids gave good recovery for TCB. However, the analytical precision for the unspiked waste was somewhat worse (25% relative standard deviation) than for the other samples.

TABLE 28. ANALYTICAL RESULTS FOR EOX IN SOLIDS$^{(a)}$

Matrix	Spike Compound	Spike Level (µg/g) as Cl$^-$	Amount OX Found (µg/g) as Cl$^-$				SD	Average Recovery (%)
			Rep 1	Rep 2	Rep 3	Av		
Process Blank	--	--	2	2	1	2	1	--
Clean Soil	--		6	4	4	5	1	--
Clean Soil	Sodium chloride	100,000	12	10	10	11	1	--
Clean Soil	1,2,4-Trichlorobenzene	5.8	10	8	10	9	1	69
Clean Soil	1,2,4-Trichlorobenzene	29	28	42	36	35	7	103
Clean Soil	2,4,6-Trichloroaniline	26	16	22	22	20	3	58
Clean Soil	2,4,6-Trichlorophenol	25	16	16	20	17	2	48
Clean Soil$^{(b)}$	2,4,6-Trichlorophenol	25	20	18	20	19	1	56
Aniline Solids	--	0	840	820	840	830	12	--
Aniline Solids	1,2,4-Trichlorobenzene	500	1400	1300	1350	1350	50	104
Landfill Solid Waste	--	0	34	26	18	26	8	--
Landfill Solid Waste	1,2,4-Trichlorobenzene	30	50	48	56	51	4	83
FeCl$_2$ Spent Catalyst$^{(c)}$(First extraction)		0	8600	8300	8400	8400	160	--
FeCl$_2$ Spent Catalyst$^{(c)}$(Second extraction)		0	2600	1900	1800	2100	270	--
FeCl$_2$ Spent Catalyst(Third extraction)		0	1100	900	1000	1000	100	--
FeCl$_2$ Spent Catalyst$^{(d)}$	--	0	8000	7500	6900	7500	550	--
Drying Bed Solids	--	0	120	80	69	90	27	--
Drying Bed Solids	1,2,4-Trichlorobenzene	170	280	230	250	250	25	94

(a) All results are reported on a dry weight basis.
(b) Sample adjusted to pH 2 before extraction.
(c) Only 100 mg of waste extracted.
(d) First ethyl acetate extract rinsed with 1 ml of water to remove inorganic halide.
SD = Standard Deviation

The potential interference by inorganic chloride was investigated. As shown in Table 28, the addition of sodium chloride at the 100-mg/g level to the "clean" soil sample did not result in a substantial increase in the EOX level. Extraction of 1 M solutions of $FeCl_2$ and $MnCl_2$ also did not yield detectable EOX levels. However, $HgCl_2$ was found to extract readily into ethyl acetate from water; and, therefore, is a potential interference in the method. No other inorganic halide salts are proven interferences, although such interferences may exist. Washing the ethyl acetate extract containing $HgCl_2$ with 1 mL of 1 M $AgNO_3$ solution was effective in removing virtually all of the inorganic chloride. Therefore, in cases where inorganic halide is present in the extract, the $AgNO_3$ precipitation procedure can be employed to eliminate the interference.

In order to assess the MDL, seven replicates of a process blank and a 15-µg/g (TCB as Cl^-) process spike were analyzed on the DX-20. The data obtained are shown in Table 29. Based on the spiked process blank data, the MDL was determined to be approximately 10 µg/g using the EMSL protocol shown in Appendix B (54).

Based on these data, the EOX/solids surrogate method appears to work quite well. However, because of the large diversity of solid-sample types, this method should not be assumed to be accurate for uncharacterized samples without further validation work being carried out. Alternate extraction solvents and other method modifications may be useful for many applications.

TABLE 29. PRECISION OF THE EOX SOLID PROCEDURE

Sample	Spike Level (µg/g) as Cl^-	Amount OX Found (µg/g) as Cl^-								SD	Recovery (%)
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Av		
Process Blank	0	8	8	12	12	20	18	14	13	5	—
Spiked Process Blank (a)	15	26	18	26	22	22	20	22	23	3	66

(a) Spiked with 1,2,4-trichlorobenzene.

SD Standard deviation

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APPENDIX A

METHOD FOR PURGEABLE ORGANIC HALIDES (POX)

1. Scope and Application

1.1 This method is to be used for the determination of Purgeable Organic Halides (POX) as Cl^-. POX is defined as the sum of those organic halides which are purged and detected by pyrolysis/microcoulometry under the conditions specified in this method. POX includes but is not limited to the priority pollutant organic halides specified in EPA Method 601(1). Purgeable organic halides containing chlorine, bromine, or iodine are detected. However, fluorine containing species are not detected by this method.

1.2 This method has been evaluated for drinking water, POTW wastewater, and industrial wastewater.(2,3)

1.3 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under applicable regulations.

1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

1.5 Since this method does not identify individual POX components, it is advisable that compound specific methods (e.g., EPA methods 601 or 624) be employed to determine the individual POX components present in samples exhibiting significant POX levels, unless the nature of the sample is already known.

2. Summary of Method

2.1 A 5-mL or 10-mL aliquot of a water sample that has been protected against the loss of volatiles by the elimination of headspace in the sampling container is transferred to a purging vessel. If maximum sensitivity is desired and the sample does not foam excessively, a 10-mL aliquot may be analyzed. Otherwise a 5-mL aliquot should be analyzed. The organic halides are purged into a pyrolysis furnace using a stream of CO_2 and the hydrogen halide (HX) pyrolysis product is determined by microcoulometric titration.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.1.3 The use of non-TFE (polytetrafluoroethylene) plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purge gas stream should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly solvents such as methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

3.4 All operations should be carried out in an area where halogenated solvents, such as methylene chloride, are not being used.

3.5 Residual free chlorine will interfere in the method. Therefore, free chlorine must be destroyed by the addition of sodium sulfite immediately after sampling.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material-handling data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety have been identified(4-6) for the information of the analyst.

4.2 The following POX compounds have been tentatively classified as known or suspected, human or mammalian carcinogens: carbon tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only.)

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial - 25-mL capacity or larger, equipped with a screw cap with hole in center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

5.1.2 Septum - Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C for 1 hour before use.

5.2 Dohrman microcoulometric-titration system DX-20, or equivalent, containing the following components:

5.2.1 Purging device

5.2.2 Pyrolysis furnace

5.2.3 Titration cell

A general description of the analytical system is shown in Figure 1.

5.3 Strip chart recorder.

5.4 Syringes - 5-mL or 10-mL glass hypodermic with Luerlok tip (2 each).

5.5 Microsyringes - 10,25 µL with .006 inch needle.

5.6 Syringe valve - 2 way, with Luer ends.

6. Reagents

6.1 Sodium sulfite - ACS, granular.

6.2 Carbon dioxide - gas, 99.9% purity.

6.3 Oxygen - 99.9% purity.

6.4 Methanol - Pesticide quality or equivalent.

6.5 Chloroform - ACS reagent grade.

6.6 70% Acetic acid in water - dilute 7 volumes of acetic acid with 3 volumes of water.

6.7 Chloroform solution, stock (1 µL = 10 µg Cl) - Prepare a stock solution by delivering accurately 760 µL (1120 mg) of chloroform into a 100-mL volumetric flask containing approximately 90 mL or methanol. Dilute to volume with methanol.

6.8 Chloroform solution, calibration (1 µL = 100 ng Cl) - Dilute 1 mL of the chloroform stock solution to 100 mL with methanol.

6.9 Chloroform performance standard (100 µg/L) - Prepare an aqueous standard by injecting 100 µL of the chloroform calibration standard (100 ng/µL) into a volumetric flask containing 100 mL of water. Mix and store in a bottle with zero headspace. Analyze within two hours after preparation.

6.10 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

6.11 Sodium chloride calibration standard (1 µg Cl^-/µL) Accurately weigh 0.1648 g of sodium chloride into a 100-mL volumetric flask. Dilute to volume with reagent water.

7. Calibration

7.1 Assemble the sparging/pyrolysis/microcoulometric titration apparatus shown in Figure 1 in accordance with the manufacturer's specifications. Typically a CO_2 flow of 150 mL/minute and a sparger temperature of 45 ± 5°C are employed. The pyrolysis furnace should be set at 800 ± 10° C. *Attach the titration cell* to the pyrolysis tube outlet and fill with electrolyte (70% acetic acid).

7.2 Turn on the instrument and allow the gas flows and temperatures to stabilize. When the background current of the titration cell has stabilized the instrument is ready for use.

7.3 Calibrate the microcoulometric titration system for Cl^- detection by injecting various amounts of the sodium chloride calibration standard directly into the titration and integrating the response using the POX integration mode. If desired the analog output of the titration cell can be displayed on a stripchart recorder. The range of sodium chloride amounts should cover the range of expected sample concentrations and should always be less than 80 μg Cl^-. Over the range 1 - 80 μg Cl^- the integrated response should read within 2% or 0.05 μg (whichever is larger) of the quantity injected. If this calibration requirement is not met then the instrument sensitivity parameters should be adjusted according to the manufacturer's specifications to achieve accurate response.

7.4 Check the performance of the entire analytical system by analyzing three 5-mL aliquots of a freshly prepared standard.

The mean of these three analyses should be 0.4 - 0.55 μg Cl and the percent relative standard deviation should be 5% or less. If these criteria are not met the system should be checked as described in the instrument maintenance manual in order to isolate the problem.

7.5 Analyze a blank reagent water sample each day. If the integrated response is greater than 0.05 μg Cl^-, then the system should be checked for sources of contamination.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a chloroform spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check sample concentrate in methyl alcohol 500 times more concentrated than the selected concentration.

8.2.2 Using a syringe, add 10 µL of the check sample concentrate to each of a minimum of four 5-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (S), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values measured in Section 8.2.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.2.5 If specific POX compounds other than chloroform are known to be present in substantial quantities in the matrix of interest these compounds should be evaluated separately through steps 8.2.1 to 8.2.4.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3 s

Lower Control Limit (LCL) = R - 3 s

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.(7)

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.

8.4 The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2.

If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 11.3. The laboratory should monitor the frequency of data so qualified to ensure that is remains at or below 5%.

8.5 Each day, the analyst must demonstrate through the analysis of reagent water, that interferences from the analytical system are under control.

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until analysis. If the sample contains free or combined chlorine, add sodium sulfite preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. EPA methods 330.4 and 330.5 may be used for measurement of residual chlorine.(8) Field test kits are available for this purpose.

9.2 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for 1 minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 All samples must be analyzed within 14 days of collection.(9)

10. Sample Analysis

10.1 Calibrate and check system performance daily as described in Section 7.

10.2 Allow sample to come to ambient temperature prior to introducing it into the syringe. Remove the plunger from a 5-mL or 10-mL syringe and attach a closed syringe valve. If maximum sensitivity is desired and the sample does not foam excessively, a 10-mL sample aliquot may be analyzed. Otherwise 5-mL aliquots should be used. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data or for intended duplicate analysis.

10.3 Attach the syringe valve assembly to the syringe valve on the purging device. Place the pyrolysis/microcoulometer system in the POX integration mode to activate integration system. Immediately open the syringe valves and inject the sample into the purging chamber.

10.4 Close both valves and purge the sample for 10 minutes.

10.5 After integration is complete open the syringe valves and withdraw the purged sample. Flush the syringe and purging device with reagent water prior to analyzing other samples.

10.6 If the integrated response exceeds the working range of the instrument, prepare a dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

11. Calculations

11.1 Determine the POX concentration in the sample as follows:

$$\text{POX Concentration, } \mu g/L \text{ as } Cl^- = \frac{Qs}{V} \times 1000$$

where:

Q_s = Quantity of POX as µg of Cl^- in the sample aliquot

V = Volume of sample aliquot in mL.

11.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

11.3 For samples processed as part of a set where the spiked sample recovery falls outside of the control limits which were established according to Section 8.3, data for the affected parameters must be labeled as suspect.

11.4 If bromine compounds are known to be the predominant species present the data for µg/L as Br should be calculated as follows:

$$\mu g/L \text{ as } Br^- = \frac{80}{35.5} \times \mu g/L \text{ as } Cl^-$$

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water(3). Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.2 This method is recommended for use in the concentration range from the MDL up to 1000 x MDL.

12.3 In a single laboratory (Battelle Columbus Laboratories), using wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained.(3)

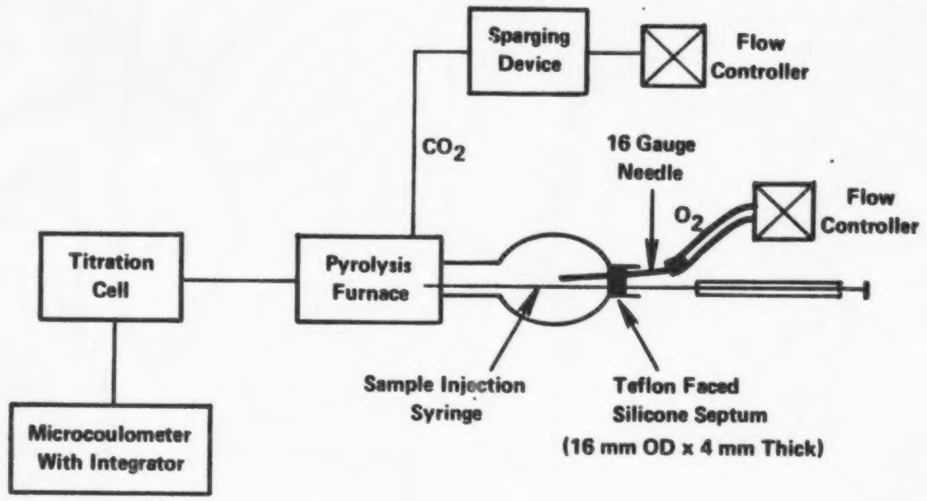
Sparging Device
Flow Controller
CO_2
16 Gauge Needle
O_2
Flow Controller
Titration Cell
Pyrolysis Furnace
Sample Injection Syringe
Teflon Faced Silicone Septum (16 mm OD x 4 mm Thick)
Microcoulometer With Integrator

Figure 1. System for determining organic halides in solvent extracts.

TABLE 1. PRECISION AND ACCURACY DATA FOR SELECTED PURGEABLE ORGANIC HALIDES *

Compound	Dose μg/L	Dose as μg/L of Cl⁻	Average Percent Recovery	Standard Deviation	MDL**	Number of Replicates
Chloroform	13	11	100	14	4.5	7
Trichloroethene	14	10	60	11	2.2	7
Tetrachloroethene	14	10	50	20	3.2	7
Chlorobenzene	25	8	38	20	2.0 #	7

* Ten milliliter aliquot of spiked reagent water analyzed.

** Calculated MDL as defined in Section 12.1.

# Practical MDL probably greater (approximately 5 to 6 μg/L) due to low recovery.

TABLE 2. PRECISION AND ACCURACY DATA FOR VARIOUS WATER SAMPLES*

Sample	Spike Component	Background Level µg/L as Cl	Spike Level		Average Percent Recovery	Standard Deviation	Number of Replicates
			µg/L	µg/L as Cl^-			
POTW Sewage	Chloroform	68	32	29	128	5	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	114	510	460	77	7	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	32	1680	1500	50	4	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	171	5050	4500	87	12	3
Solid Waste Leachate	1,1-Dichloroethane	171	1130	800	44	2	3
Industrial Wastewater**	Methylene Chloride	510	145	120	65	12	3

* Five milliliter sample aliquots analyzed.

** Diluted 200:1 prior to analysis. Values for this sample are in mg/L for original sample.

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8. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Ohio 45268, March 1979.

9. "Preservation and Maximum Holding Time for the Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Ohio 45268. In preparation.

APPENDIX B

DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte. The statistical basis for this procedure is described in the literature (54).

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:
   - (a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.
   - (b) Three times the standard deviation of replicate instrumental measurements of the reagent water.
   - (c) The area of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.
   - (d) Instrumental limitations.

   It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interference concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interference). The interference concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample containing a lower level of analyte in the same matrix if possible.

(2) The untreated sample may be used for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each aliquot through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This step will: (1) prevent repeating this entire procedure when the costs of analyses are high and (2) ensure that the procedure is being conducted at the correct concentration. It is quite possible that an incorrect MDL could be calculated from data obtained at many times the real MDL and the level of analyte would be less than five times the calculated method detection limit. To ensure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left\{\left(\sum_{i=1}^{n} X_i^2\right) - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right\}$$

$$S = (S^2)^{1/2}$$

where the x_i, i=1 to n are the analytical results in the final method reporting units obtained from the n sample aliquots and referes to the sum of th X values from i=1 to n.

6. a.) Compute the MDL as follows:

$$MDL = t_{(n-1,.99)} \; (S)$$

where:

MDL = the method detection limit

$t_{(n-1,.99)}$ = the Student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

b.) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (X^2/df):

LCL = 0.64 MDL
UCL = 2.20 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

a.) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with step 4.

b.) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2

from the previous MDL calculation to compute the F-ratio. The F-ratio is formed by substituting the largest S^2 of the two into the numerator S and the other into the denominator S. The computed F-ratio is then compared with the F-ratio found in the table which is 4.28 as follows:

$$\text{if} \quad \frac{S_A^2}{S_B^2} < 4.28,$$

then compute the pooled standard deviation by the following equation:

$$S_{\text{pooled}} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{1/2}$$

$$\text{if} \quad \frac{S_A^2}{S_B^2} > 3.05,$$ respike at the last calculated MDL and process the samples through the procedure starting with step 4.

c.) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$\text{MDL} = 2.681 \ (S_{\text{pooled}})$

where 2.681 is equal to $t_{(12, \ = .99)}$.

d.) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

Table of Student's t Values at the 99 Percent Confidence Level

Number of Replicates	Degrees of Freedom (n-1)	$t_{(n-1,.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

APPENDIX C

TOTAL ORGANIC HALIDE

Method 450.1

1. Scope and Application

   1.1 This method is to be used for the determination of Total Organic Halides as Cl^- by carbon adsorption, and requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/L. Organic halides as used in this method are defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine containing species are not determined by this method.

   1.2 This is a microcoulometric-titration detection method applicable to the determination of the compound class listed above in drinking and ground waters, as provided under 40 CFR 265.92.

   1.3 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 260.21.

   1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcolumeter and in the interpretation of the results.

2. Summary of Method

   2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides, and is then pyrolyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

4. Safety

The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material-handling data sheets should also be made available to all personnel involved in the chemical analysis.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only).

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab-sample bottle - Amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400°C before use, to minimize contamination.

5.2 Adsorption System

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

5.2.2 Adsorption columns - pyrex, 5 cm long X 6-mm OD X 2-mm ID.

5.2.3 Granular Activated Carbon (GAC) - Filtrasorb-400, Calgon-APC, or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000-ng Cl^- equivalent or less.

5.2.4 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

5.2.5 Column holders (available from Dohrman).

5.2.6 Volumetric flasks - 100-mL, 50-mL.

A general schematic of the adsorption system is shown in Figure 1.

5.3 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

5.3.1 Boat sampler.

5.3.2 Pyrolysis furnace.

5.3.3 Microcoulometer with integrator.

5.3.4 Titration cell.

A general description of the analytical system is shown in Figure 2.

5.4 Strip-Chart Recorder.

6. Reagents

6.1 Sodium sulfite - 0.1 M, ACS reagent grade (12.6 g/L).

6.2 Nitric acid - concentrated.

6.3 Nitrate-Wash Solution (5000 mg NO_3^-/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-litre volumetric flask and diluting to volume with reagent water.

6.4 Carbon dioxide - gas, 99.9% purity.

6.5 Oxygen - 99.9% purity.

6.6 Nitrogen - prepurified.

6.7 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.8 Trichlorophenol solution, stock (1 µL = 10 µg Cl^-) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.9 Trichlorophenol solution, calibration (1 µL = 500 ng Cl^-) - Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

6.10 Trichlorophenol standard, instrument-calibration - First, nitrate wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µL of the calibration solution.

6.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/L) - Prepare a adsorption-efficiency standard by injecting 10 µL of stock solution into 1 liter of reagent water.

6.12 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

6.13 Blank standard - The reagent water used to prepare the calibration standard should be used as the blank standard.

7. Calibration

7.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 mL of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2 Nitrate-wash blanks (Method Blanks) - Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations.

7.2.1 The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

8. Sample Preparation

8.1 Special care should be taken in the handling of the sample to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

8.2 Reduce residual chlorine by the addition of sulfite (1 mL of 0.1 M per liter of sample). Addition of sulfite should be done at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4°C without headspace.

8.3 Adjust pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

9. Adsorption Procedure

9.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

9.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min. NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/L; 50 mL for 501 to 1000 µg/L, and 25 mL for 1001 to 2000 µg/L.

9.3 Wash the columns-in-series with 2 mL of the 5000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

10. Pyrolysis Procedure

10.1 The contents of each column is pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

10.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to assure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

NOTE: The quartz sampling boat should have been previously muffled at $800^{o}C$ for at least 2 to 4 minutes as in a previous analysis, and should be cleaned of any residue by vacuuming.

10.3 Transfer the contents of each column to the quartz boat for individual analysis.

10.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCT-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

10.5 Position the sample for 2 minutes in the $200^{o}C$ zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

10.6 After 2 minutes, advance the boat into the $800^{o}C$ zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 minutes to complete.

11. Detection

The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

12. Breakthrough

Because the background bias can be of such an unpredictable nature, it can be especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10-percent of the two-column total measurement. If the 10-percent figure is exceeded, one of three events can have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained - in which case taking a smaller sample may be necessary; or channeling or some other failure occurred - in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun. Because knowing which event has occurred may not be possible, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analyses that is rejected should be repeated whenever sample is available. In the event that the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

13. Quality Control

13.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by the analysis of appropriate quality-control check samples.

13.2 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

13.3 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

14. Calculations

OX as Cl^- is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

C_1 = µg Cl^- on the first column in series

C_2 = µg Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in L

15. Accuracy and Precision

These procedures have been applied to a large number of drinking-water samples. The results of these analysis are summarized in Tables I and II.

16. Reference

Dressman, R., Najar, G., Redzikowski, R., paper presented at the Proceedings of the American Water Works Association Water Quality Technology Conference, Philadelphia, Dec. 1979.

TABLE I

PRECISION AND ACCURACY DATA FOR MODEL COMPOUNDS

Model Compound	Dose µg/L	Dose as µg/L Cl	Average % Recovery	Standard Deviation	No. of Replicates
$CHCl_3$	98	88	89	14	10
$CHBrCl_2$	160	106	98	9	11
$CHBr_2Cl$	155	79	86	11	13
$CHBr_3$	160	67	111	8	11
Pentachlorophenol	120	80	93	9	7

TABLE II

PRECISION DATA ON TAP WATER ANALYSIS

Sample	Avg. halide ug Cl/L	Standard Deviation	No. of Replicates
A	71	4.3	8
B	94	7.0	6
C	191	6.1	4

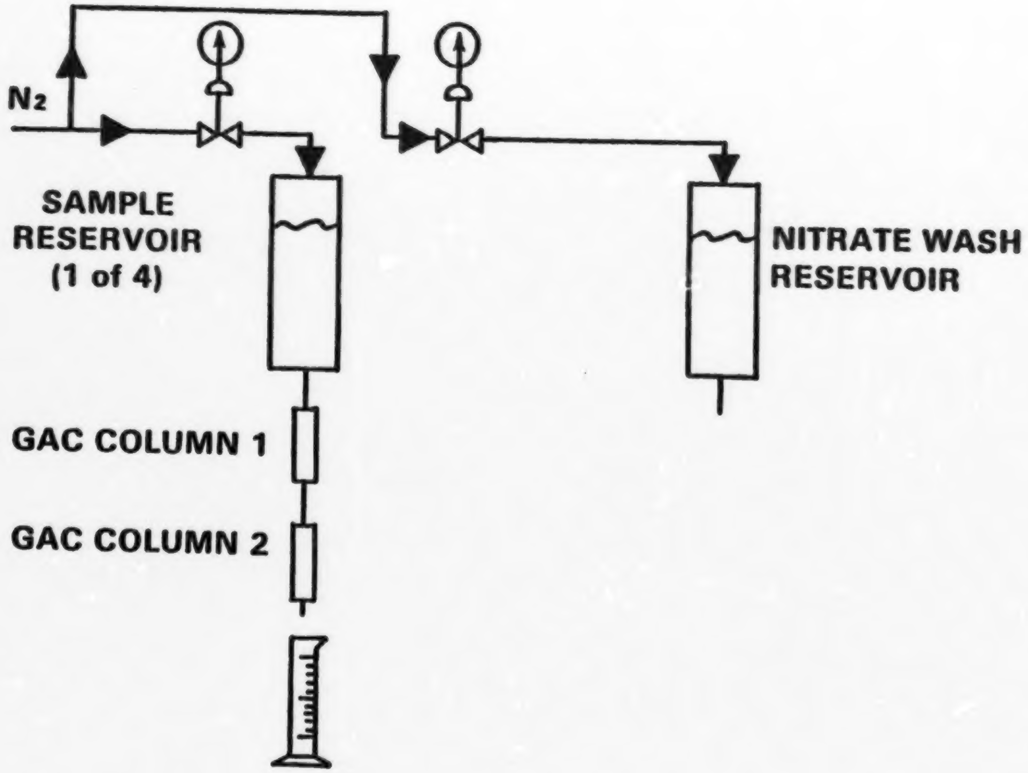
N₂
SAMPLE RESERVOIR (1 of 4)
NITRATE WASH RESERVOIR
GAC COLUMN 1
GAC COLUMN 2

Figure 1. Adsorption Schematic

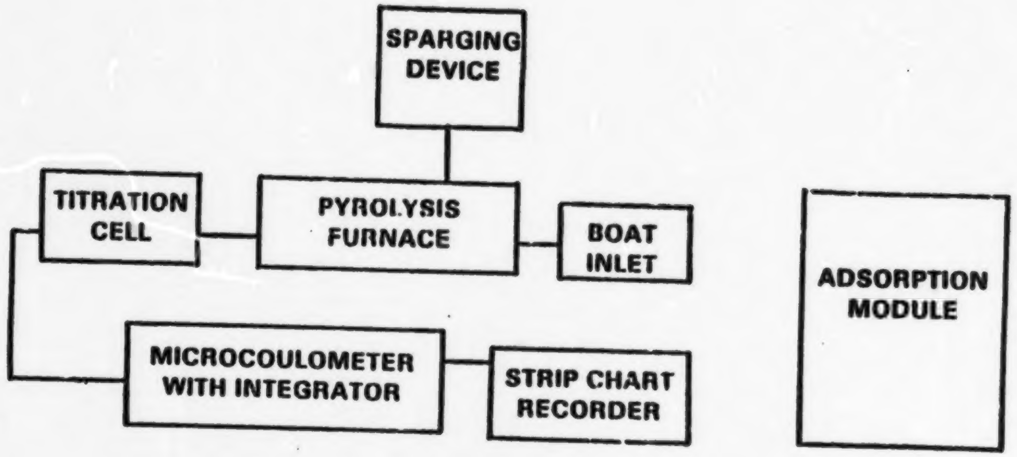
SPARGING DEVICE
TITRATION CELL
PYROLYSIS FURNACE
BOAT INLET
ADSORPTION MODULE
MICROCOULOMETER WITH INTEGRATOR
STRIP CHART RECORDER

Figure 2. CAOX Analysis System Schematic

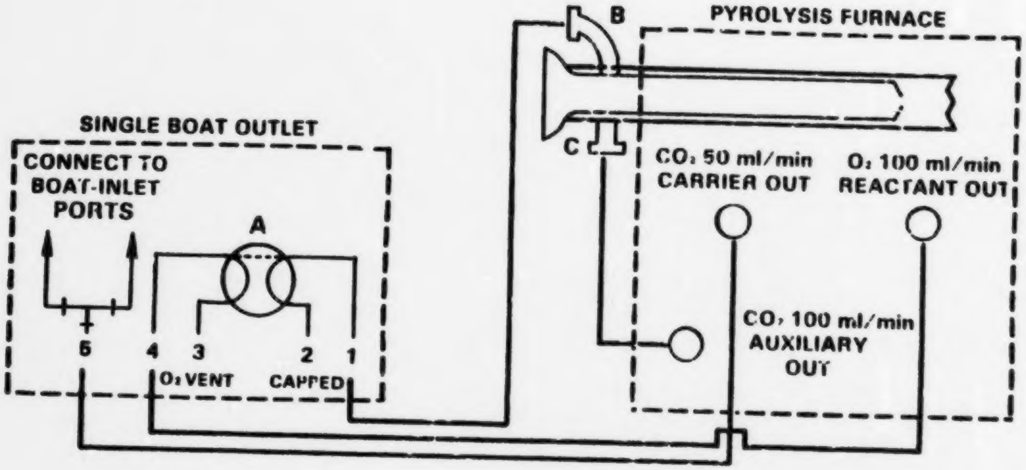
B
PYROLYSIS FURNACE
SINGLE BOAT OUTLET
CONNECT TO BOAT-INLET PORTS
A
C
CO_2 50 ml/min CARRIER OUT
O_2 100 ml/min REACTANT OUT
CO_2 100 ml/min AUXILIARY OUT
5
4
3
2
1
O_2 VENT
CAPPED

Figure 3. Rear view plumbing schematic for MCTS-20 system. Valve A is set for first-stage combustion, O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

APPENDIX D

METHOD FOR EXTRACTABLE ORGANIC HALIDES (EOX) IN SOLIDS

1. Scope and Application 1.1

1.1 This method is to be used for the determination of extractable organic halides (EOX) as Cl^- in solids. EOX is defined as the sum of those organic halides which are extracted and detected by pyrolysis/microcoulometry under the conditions specified in this method. EOX includes but is not limited to the priority pollutant organic halides specified in EPA Method 624 and 625 (1,2). Extractable organic halides containing chlorine, bromine, or iodine are detected. However, fluorine containing species are not detected by this method.

1.2 This method has been evaluated for solid wastes, soils, and suspended solids isolated from industrial wastewater (2).

1.3 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 260.21.

1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis microcoulometer and in the interpretation of the results.

1.5 Since this method does not identify individual components, it is advisable that compound specific techniques be employed to determine the individual components present in samples exhibiting significant EOX levels, unless the nature of the sample is already known.

2. Summary of Method 2.1

A 1-gram aliquot of a solid sample is extracted with ethyl acetate by sonification to isolate organic halides. A 25-μL aliquot of the extract is injected into a pyrolysis furnace using a stream of CO_2/O_2 and the hydrogen halide (HX) pyrolysis product is determined by microcoulometric titration.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.1.3 The use of non-TFE (polytetrafluoroethylene) plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purge gas stream should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly solvents such as methylene chloride) through the septum seal into the sample during shipment and storage.

3.3 All operations should be carried out in an area where halogenated solvents, such as methylene chloride, are not being used.

3.4 Certain inorganic halide salts (e.g., mercuric chloride) will be extracted, and therefore interfere to some extent.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals used in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety have been identified (4-6) for the information of the analyst.

4.2 Certain EOX compounds are tentatively classified as known or suspected human or mammaliam carcinogens. These include (but are not limited to) carbon tetrachloride, chloroform, 1,4-dichlorobenzene, vinyl chloride, polychlorinated biphenyls, α-BHC, β-BHC, δ-BHC, γ-BHC, and 4,4'-DDT. Primary standards of these compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handled high concentrations of these toxic compounds.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only.)

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial - 25-mL capacity or larger, equipped with a screw cap with hole in center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

5.1.2 Septum - Teflon-faced silicone (Pierce #12622 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C for 1 hour before use.

5.2 Modified Dohrmann microcoulometric-titration system DX-20, or equivalent, containing the following components:

5.2.1 Solvent injection system
5.2.2 Pyrolysis furnace
5.2.3 Titration cell.

A general description of the analytical system is shown in Figure 1. The septum injection system replaces the boat entry system normally provided with the DX-20. Bypass DX-20 flow controllers, using separate flow controllers for O_2 and CO_2 continuous flow.

5.3 Microsyringes - 10,25 μL with 26 gauge 4-inch-long needle.

5.4 Laboratory centrifuge to hold 15-ml conical centrifuge tubes.

5.5 Sonic bath or sonic probe to fit 2-dram vial. A power level of at least 200 watts is required.

5.6 Centrifuge Tubes - 15 ml, conical, with teflon-lined screw caps.

5.7 Vials - 2 dram, with teflon-lined screw caps.

5.8 Metal spatula

5.9 Disposable Pasteur pipettes and bulbs.

6. Reagents

6.1 Carbon dioxide - gas, 99.9% purity.

6.2 Oxygen - 99.9% purity.

6.3 Ethyl acetate - Pesticide quality or equivalent.

6.4 1,2,4-Trichlorobenzene - 99%.

6.5 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.6 Trichlorobenzene solution, stock (1 μL = 1 μg Cl) - Prepare a stock solution by delivering accurately 117 μL (170 mg) of trichlorobenzene into a 100-mL volumetric flask and dilute to volume with ethyl acetate.

6.7 Trichlorobenzene solution, calibration (1 μL = 100 ng Cl) - Dilute 10 mL of the trichlorobenzene stock solution to 100 mL with ethyl acetate.

6.8 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

6.9 Sodium chloride calibration standard (1 μg Cl-/μL). Accurately weigh 0.1648 g of sodium chloride into a 100-mL volumetric flask. Dilute to volume with reagent water.

7. Calibration

7.1 Assemble the solvent injection/pyrolysis/microcoulometric titration apparatus shown in Figure 1 in accordance with the manufacturer's specifications and the modifications shown. Adjust the CO_2 flow to 300 mL/minute and the O_2 flow to 100 mL/minute using the auxiliary flow controllers (bypass the DX-20 flow controllers). The pyrolysis furnace should be set at 800 ± 10°C. Attach the titration cell to the pyrolysis tube outlet and fill with electrolyte (70% acetic acid).

7.2 Turn on the instrument and allow the gas flows and temperatures to stabilize. When the background current of the titration cell has stabilized the instrument is ready for use.

7.3 Calibrate the microcoulometric titration system for Cl- detection by injecting various amounts of the sodium chloride calibration standard directly into the titration cell and integrating the response using the POX integration mode. The range of sodium chloride amounts should cover the range of expected sample concentrations and should always be less than 80 µg Cl-. Over the range 1 - 80 µg Cl- the integrated response should read within 2% or 0.05 µg (whichever is larger) of the quantity injected. If this calibration requirement is not met then the instrument sensitivity parameters should be adjusted according to the manufacturer's specifications to achieve accurate response.

7.4 Check the performance of the entire analytical system by injecting three 25-µL aliquots of the trichlorobenzene calibrate standard into the furnace at a rate of 1 mL/second. The mean of these three analyses should be 2.2 - 2.8 µg Cl and the percent relative standard deviation should be 5% or less. If these criteria are not met the system should be checked as described in the instrument maintenance manual in order to isolate the problem.

7.5 Perform a blank ethyl acetate injection (25-µL) each day. If the integrated response is greater than 0.1 µg Cl-, then the system should be checked for sources of contamination.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a trichlorobenzene spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check sample concentrate in ethyl acetate 100 times more concentrated than the selected concentration.

8.2.2 Place a minimum of six 1-gram aliquots of an uncontaminated soil sample in 2-dram vials. Spike four of the samples with 10 µL of the check sample, cap the vials, shake vigorously, and allow the spike to equilibrate with the sample by standing overnight. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (S), for the results. Soil background corrections must be made before R and S calculations are performed.

8.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values measured in analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 11.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Each day, the analyst must demonstrate, through the analysis of uncontaminated soil, that interferences from the analytical system are under control.

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until analysis.

9.2 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle as completely as possible to minimize headspace until time of analysis.

9.3 If the analysis is to be conducted on suspended solids from a wastewater sample, isolate the solids by centrifugation, weigh the wet solids, and analyze immediately. Determine the dry weight of a separate portion of the wet solids by heating overnight at 110°C.

10. Sample Analysis

10.1 Calibrate and check system performance daily as described in Section 7.

10.2 Transfer a 1-gram aliquot of the solid sample to a 2-dram vial using a metal spatula. Add one milliliter of reagent water and five milliliters of ethyl acetate to the sample and cap tightly.

10.3 Shake the sample vigorously for thirty seconds and then place the vial in a sonic bath filled with water to a level of ∿1 inch, or agitate the suspension directly using a sonic probe, if available. Sonify the sample for 15 minutes if using a sonic bath or 5 minutes if using a sonic probe.

10.4 Allow the suspension to settle for 10 minutes and then transfer the upper layer (ethyl acetate) to a 15-mL conical centrifuge tube. Cap the tube and centrifuge at approximately 1000 x g for five minutes.

10.5 Transfer the ethyl acetate layer to a clean 2-dram vial, cap, and store refrigerated until analyzed.

10.6 For analysis withdraw a 5 to 25-μL aliquot of the ethyl acetate into a microsyringe having a 4-inch long needle. Place the pyrolysis/microcoulometer system into the POX integration mode and immediately pierce the septum and position the tip of the microsyringe into the furnace. Inject the sample at a rate of approximately 1 μL/second and withdraw the needle when sample injection is complete.

10.7 After the 10-minute integration cycle is complete record the integrated response. If the response exceeds the working range of the instrument repeat the analysis after dilution of the extract with reagent grade ethyl acetate.

11. Calculations

11.1 Determine the EOX concentration in the sample as follows:

$$\text{EOX Concentration, } \mu g/g \text{ as Cl-} = \frac{Q_S \times V_E}{W_S \times V_I} \times 1000$$

where:

Q_S = Quantity of EOX as μg of Cl- in the aliquot injected.

V_I = Volume of aliquot injected in μL.

V_E = Total volume of extract in mL.

W_S = Weight of sample extracted in grams.

11.2 Report results in micrograms per gram. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

11.3 For samples processed as part of a set where the spiked sample recovery falls outside of the control limits which were established according to Section 8.3, data for the affected parameters must be labeled as suspect.

11.4 If the aqueous portion of a water sample, from which the suspended solids are being analyzed, is expected to contain high levels of organic halide, a 1-mL aliquot of the centrifuged sample should be analyzed. The solids data must then be corrected using the following equation:

$$\text{EOX (corrected)} = \text{EOX}_S - \text{EOX}_W \times \frac{W_S}{W_D}$$

where:

EOX_S = EOX in wet solids, µg/g as Cl

EOX_W = EOX in water sample, µg/g as Cl

W_S = Wet weight of solids, grams

W_D = Dry weight of solids, grams

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. An MDL of 10 µg/g was obtained using injected ethyl acetate standards (3). The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.2 This method is recommended for use in the concentration range from the MDL up to 1000 x MDL.

12.3 In a single laboratory (Battelle Columbus Laboratories), using solid spiked at various levels, the average recoveries presented in Table 1 were obtained (3).

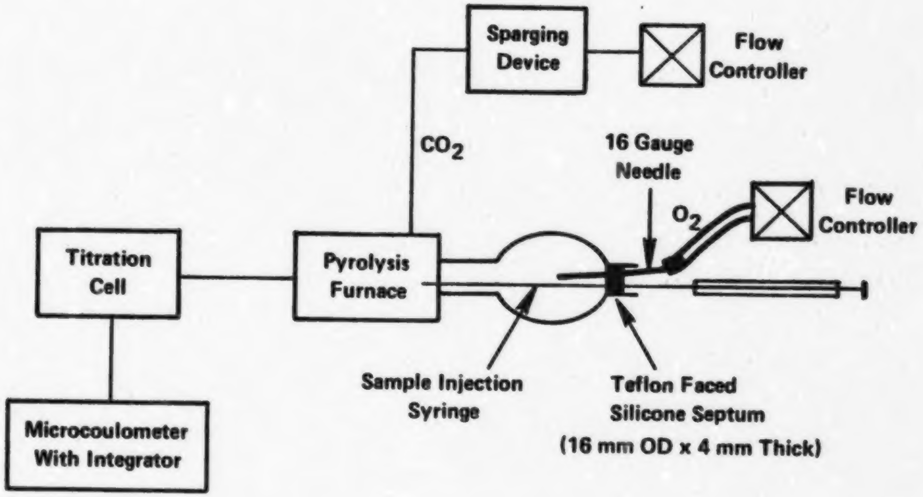
Sparging Device
Flow Controller
CO_2
16 Gauge Needle
O_2
Flow Controller
Titration Cell
Pyrolysis Furnace
Sample Injection Syringe
Teflon Faced Silicone Septum (16 mm OD x 4 mm Thick)
Microcoulometer With Integrator

Figure 1. System for determining organic halides in solvent extracts.

TABLE 1. METHOD PERFORMANCE DATA FOR VARIOUS SOLID SAMPLES

Sample	Spike Compound	Spike Level		Average Percent Recovery	Standard Deviation of Recovery	Number of Replicates
		μg/g	μg/g as Cl^-			
"Clean Soil"	1,2,4-Trichlorobenzene	10	6	69	11	3
"Clean Soil"	1,2,4-Trichlorobenzene	49	29	103	20	3
"Clean Soil"	2,4,6-Trichloroaniline	47	26	58	15	3
"Clean Soil"	2,4,6-Trichlorophenol	46	25	48	11	3
Suspended Solids from Industrial Effluent	1,2,4-Trichlorobenzene	850	500	104	3	3
Solid Waste from Landfill	1,2,4-Trichlorobenzene	51	30	83	8	3
"Drying Bed" Solid Waste from Chloroethylene Manufacturing	1,2,4-Trichlorobenzene	290	170	94	10	3

REFERENCES

1. EPA Method 624, Federal Register V. 45, December 3, 1979.

2. EPA Method 624, Federal Register V. 45, December 3, 1979.

3. Surrogate Methods for Priority Pollutants in Wastewater, Contract No. 68-03-2984, Final Report, in preparation.

4. "Carcinogens - Working With Carcinogens", Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

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6. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", EPA-600/4-79-019, U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Ohio 45268, March 1979.